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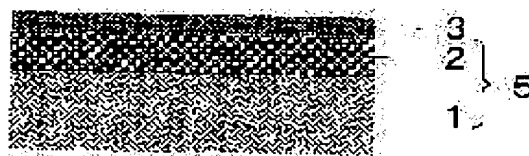
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(54) ELECTRODE BACKING AND ITS MANUFACTURING METHOD AND FUEL CELL USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a high performance electrode backing 5 and its manufacturing method in which the backing has good fuel diffusion property and good drainage compared to conventional one, also the backing suppresses penetration of catalyst layer.

SOLUTION: In the electrode backing 5 containing a porous conductive sheet 1 comprised of an inorganic conductive fiber, the surface roughness (Ra) of the surface of one side of the sheet 1 on which an electrode catalyst is applied is made not less than 2  $\mu\text{m}$  and not larger than 20  $\mu\text{m}$  by surface roughness defined in JIS B0601.



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CLAIMS

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[Claim(s)]

[Claim 1] The surface roughness of the side which prepares the electrode catalyst bed of this sheet in the electrode substrate containing the electric conduction sheet of the porosity which consists of inorganic conductivity fiber is JIS. Electrode substrate characterized by 2-micrometer or more being 20 micrometers or less by the center line average of roughness height (Ra) specified by B0601.

[Claim 2] The electrode substrate according to claim 1 characterized by preparing the inorganic conductivity matter layer in the front face of a porosity electric conduction sheet further.

[Claim 3] The electrode substrate according to claim 2 characterized by the inorganic conductivity matter having a particle-like gestalt.

[Claim 4] The electrode substrate according to claim 2 or 3 characterized by the inorganic conductivity matter being carbon material.

[Claim 5] The electrode substrate according to claim 4 characterized by carbon material being carbon black.

[Claim 6] An inorganic conductivity matter layer is an electrode substrate according to claim 2 to 5 characterized by a front-face side being dense and forming the porosity electric conduction sheet side in a rough \*\*\*\*\* unsymmetrical vesicular structure.

[Claim 7] An inorganic conductivity matter layer is an electrode substrate according to claim 6 characterized by these relation being  $1 < SA/SB \leq 2000$  when setting specific surface area of the inorganic conductivity matter by the side of SA (m<sup>2</sup>/g) and a porosity electric conduction sheet to SB (m<sup>2</sup>/g) for the specific surface area of the inorganic conductivity matter by the side of a front face.

[Claim 8] The electrode substrate according to claim 1 to 7 characterized by a porosity electric conduction sheet using inorganic conductivity fiber.

[Claim 9] The electrode substrate according to claim 8 characterized by inorganic conductivity fiber being a carbon fiber.

[Claim 10] The electrode substrate according to claim 9 characterized by a carbon fiber being what uses a polyacrylonitrile, a pitch, or a low-boiling point organic compound as a raw material.

[Claim 11] The electrode substrate according to claim 1 to 10 with which a porosity electric conduction sheet is characterized by being textile fabrics, a paper-making object, the felt, or a nonwoven fabric.

[Claim 12] The electrode substrate according to claim 1 to 11 characterized by the superintendent officer of a porosity electric conduction sheet being 10 - 220 g/m<sup>2</sup>.

[Claim 13] The manufacture approach of the electrode substrate according to claim 2 characterized by applying to the front face of a porosity electric conduction sheet the inorganic conductivity matter dispersion liquid whose viscosity is 10 or more Pa-s.

[Claim 14] The manufacture approach of the electrode substrate according to claim 2 characterized by pressing or grinding the front face of an inorganic conductivity matter layer after preparing an inorganic conductivity matter layer in the front face of a porosity electric conduction sheet.

[Claim 15] Film-electrode complex using an electrode substrate according to claim 1 to 12.

- [Claim 16] Electrochemistry equipment using an electrode substrate according to claim 1 to 12.
- [Claim 17] Water electrolysis equipment using an electrode substrate according to claim 1 to 12.
- [Claim 18] The fuel cell using an electrode substrate according to claim 1 to 12.
- [Claim 19] The polymer electrolyte fuel cell using an electrode substrate according to claim 1 to 12.
- [Claim 20] The direct methanol mold fuel cell using an electrode substrate according to claim 1 to 12.
- [Claim 21] The mobile which makes a fuel cell according to claim 18 to 20 a power source of supply.
- [Claim 22] The automobile which makes a fuel cell according to claim 18 to 20 a power source of supply.
- [Claim 23] Pocket electronic equipment which makes a fuel cell according to claim 18 to 20 a power source of supply.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the electrode substrate used for a fuel cell, its manufacture approach, etc.

[0002]

[Description of the Prior Art] A fuel cell is the low power plant of the burden to an environment at low excretions and high energy effectiveness as everyone knows. For this reason, it is in the limelight again in the rise to earth environmental protection in recent years. Compared with the conventional large-scale generation-of-electrical-energy facility, it is the power plant expected also in the future as a power plant of pocket electronic equipment, such as power plants of a mobile, such as a comparatively small-scale distributed generation-of-electrical-energy facility, an automobile, and a vessel, and a cellular phone. There is a class of a solid-state macromolecule mold, a phosphoric-acid mold, a solid acid ghost mold, a melting carbonate mold, alkali mold, etc. of fuel cells according to the class of electrolyte used. Especially, compared with other fuel cells, warm-up time of an operating temperature is short at low temperature, and a polymer electrolyte fuel cell has the descriptions which high power tends to acquire, like that it can count upon small lightweight-ization, and it is strong to vibration, and fits the power source of supply of a mobile. Furthermore, also in the polymer electrolyte fuel cell, the direct methanol mold fuel cell which supplies a direct methanol water solution to a fuel has high energy density, and it is suitable for the power source of supply of pocket electronic equipment.

[0003] The fuel cell is constituted considering the cell into which the electrolyte used as the anode with which the reaction which bears a generation of electrical energy occurs, the electrode of a cathode, and an anode and the ion conductor between cathodes was inserted with the separator between each as a unit. The electrode consists of promotion of fuel diffusion, an electrode substrate (it is also called a charge collector) which performs \*\* (\*\*\*) \*\*, and an electrode catalyst bed which actually serves as an electrochemical reaction place. For example, in the anode electrode of a polymer electrolyte fuel cell, a fuel reacts on a catalyst front face, a proton and an electron are produced, an electron is conducted to an electrode substrate, and a proton is conducted to the electrolytic proton exchange film. For this reason, it is required for an anode electrode that fuel diffusibility, electronic conduction nature, and ion conductivity should be good. On the other hand, in a cathode electrode, the proton which oxidation gas has conducted from the electrolyte on the electrode catalyst bed front face, and the electron conducted from the electrode substrate react, and water is generated. For this reason, it is also necessary to discharge efficiently the water generated with gaseous diffusion nature, electronic conduction nature, and ion conductivity.

[0004] In order to fill such a demand, various examination has so far been added to the electrode substrate. For example, the technique of a publication is reported to JP,10-261421,A or JP,11-273688,A until now as an example which raised gaseous diffusion nature.

[0005] In order to consider as the electrode substrate aiming at a gaseous diffusion disposition top, the example which prepared the layer of carbon black on the surface of the electrode substrate is indicated by these official reports. Moreover, as a conventional technique of others

of an electrode substrate (charge collector), the thing of JP,6-20710,A, JP,7-326362,A, or JP,7-220735,A is proposed. The charge collector indicated by these consists of a porous carbon plate to which it comes to bind the carbon fiber of short die length with carbon.

[0006] As mentioned above, although an electrode consists of an electrode substrate and an electrode catalyst bed, as these demand characteristics, with fuel diffusibility, electronic conduction nature, and ion conductivity, discharging the generated water efficiently is called for and, especially as for the electrode substrate, the porosity electric conduction sheet is used from the point of fuel diffusibility, electronic conduction nature, and wastewater nature. Also in such a porosity electric conduction sheet, porosity electric conduction sheets, such as textiles, a paper-like paper-making object and the felt, and a nonwoven fabric, have been used for the improvement in fuel diffusibility, and manufacture cost reduction. And applying an electrode catalyst bed to the front face of the electrode substrate which consists of such a porosity electric conduction sheet is performed.

[0007] In this electrode catalyst bed, since the catalysts which are used in addition to the above-mentioned demand characteristics are expensive noble metals, such as platinum and a ruthenium, it is required to aim at improvement in the amount of catalysts used effectively. When an electrode catalyst bed was applied to the electrode substrate which consists of the above porosity electric conduction sheets especially, the permeate lump of the electrode catalyst bed coating liquid to an electrode substrate was large, and it had become the cause by which the useless catalyst which is not used effectively because of this permeate lump increased.

[0008] By the way, although the fuel cell is expected as a power source of supply of a mobile or pocket electronic equipment, it needs a large cost cut for the extensive spread of an automobile, cellular phones, etc. Especially, since the above-mentioned noble metals are used in the catalyst particle in an electrode catalyst bed, it is very expensive, and reducing this amount of catalysts is called for strongly. For this reason, it is required to reduce the catalyst which permeates an electrode substrate and is not used effectively as much as possible. Preparing the interlayer who does not include a catalyst in the Patent Publication Heisei No. 501541 [ nine to ] official report as the technique of suppressing such a permeate lump is indicated. Here, it is indicated that a catalyst permeates and the interlayer who contains acetylene black and a proton electric conduction polymer as an electric conduction agent has effectiveness in lump prevention. However, a proton electric conduction polymer is a hydrophilic polymer, and since water is easy to be included, we are anxious about causing trouble to discharge of the generation water in a cathode.

[0009] Moreover, the surface carbon black layer of the electrode substrate which prepared the above-mentioned carbon black layer is not smooth, and the electrode catalyst bed therefore prepared on it does not become smooth. For this reason, we are anxious about the proton conductivity between proton exchange film-electrode catalyst beds worsening with not sufficient junction on an electrode catalyst bed and the proton exchange film.

[0010]

[Problem(s) to be Solved by the Invention] By suppressing a permeate lump of the catalyst of a under [ the above-mentioned technical problem, i.e., an electrode substrate, ], this invention reduces the amount of catalysts which becomes useless, and moreover, its wastewater engine performance in a cathode is good, and it aims at offering a highly efficient electrode substrate, its manufacture approach, etc. also about the proton conductivity between proton exchange film-electrode catalyst beds.

[0011]

[Means for Solving the Problem] This invention has the following configuration, in order to solve the above-mentioned technical problem.

[0012] That is, for this invention, the surface roughness of the side which prepares the electrode catalyst bed of this sheet in the electrode substrate which consists of an electric conduction sheet of the porosity containing inorganic conductivity fiber is JIS. It is characterized by 2-micrometer or more being 20 micrometers or less by the center line average of roughness height (Ra) specified by B0601.

[0013] Moreover, the manufacture approach of the electrode substrate of this invention is

characterized by applying to the front face of the above-mentioned sheet the inorganic conductivity matter dispersion liquid whose viscosity is 10 or more Pa-s.

[0014] Moreover, the electrochemistry equipment, the water electrolysis equipment, and the fuel cell of this invention are characterized by coming to apply the above-mentioned electrode substrate.

[0015] Furthermore, the mobile and pocket electronic equipment of this invention are characterized by becoming considering the above-mentioned fuel cell as a power source of supply.

[0016]

[Embodiment of the Invention] Hereafter, the gestalt of desirable operation of this invention is explained with reference to a drawing.

[0017] Drawing 1 thru/or drawing 3 are drawings of longitudinal section of various examples where the electrode substrate 5 of this invention is used. Drawing 1 the mode by which the inorganic conductivity matter layer 2 was formed in the front face of the electrode substrate 5 of this invention Drawing 3 shows the film-electrode complex (MEA) of a mode with which the mode by which, as for drawing 2, the laminating of the electrode catalyst bed 3 was further carried out to the front face of the inorganic conductivity matter layer 2 of the electrode substrate 5 of drawing 1 was prepared in the electrode substrate 5 with an electrode catalyst bed of drawing 3 by both sides centering on the proton exchange film 4. In addition, although the electrode substrate 5 of this invention says what usually formed the inorganic conductivity matter 2 in one side of the porosity electric conduction sheet 1 like drawing 1, although illustration was omitted, the direct electrode catalyst bed 3 may be formed on the porosity electric conduction sheet 1, and such a thing is also contained in the electrode substrate of this invention.

[0018] In drawing 1, although the porosity electric conduction sheet 1 does not bear diffusion of a fuel, and electronic conduction and is not limited especially, it is desirable to use the conductive matter as a main component, for example. As this conductive matter, carbon material, such as a baking object from a polyacrylonitrile, a baking object from a pitch, a graphite, and expanded graphite, stainless steel, molybdenum, titanium, etc. are illustrated. Although the shape of fibrous or a particle etc. is not limited, the inorganic conductivity fiber of a fibrous gestalt of especially the gestalt of the conductive matter is desirable from the point of the electrode engine performance. When using for electrochemistry equipments, such as a fuel cell, especially, it is desirable to use a carbon fiber from the point of corrosion and electric resistance.

[0019] As for the material, as a carbon fiber, what uses a polyacrylonitrile (PAN), a pitch, or a low-boiling point organic compound as a raw material is desirable. Benzene, naphthalene, Creotall oil, etc. can be illustrated as a low-boiling point organic compound. A PAN system carbon fiber is desirable also especially in these. As for a PAN system carbon fiber, compared with a pitch based carbon fiber, whenever [ compressive-strength and \*\*\*\* breaking extension ] is large, and it cannot break easily. This is considered to be based on the difference of crystallization of the carbon which constitutes a carbon fiber. In order to obtain the carbon fiber into which it is hard to break, the heat treatment temperature of a carbon fiber has desirable 2,500 degrees C or less, and its 2,000 degrees C or less are more desirable.

[0020] the sheet which has textile fabrics or non-woven fabric structure as a gestalt of the porosity electric conduction sheet 1 -- which structure is sufficient. After weaving the filament textile fabrics and spun yarn which come to weave the filament of inorganic conductivity fiber as textile-fabrics structure and considering as textile fabrics, the spun-yarn textile fabrics which gave conductivity can be used. After bundling a carbon fiber filament, making it a strand as an example of filament textile fabrics, mentioning the carbon fiber filament textile fabrics which come to weave this, spinning PAN system fiber as an example of spun-yarn textile fabrics, weaving this spun yarn and considering as textile fabrics, the carbon fiber spun-yarn textile fabrics which it comes to calcinate are mentioned. Moreover, as a sheet of non-woven fabric structure, sheets which have structure with irregular fiber, such as a paper-making object, felt, and a nonwoven fabric, are mentioned. A paper-making object is the structure of the thin shape

of even paper acquired by dipping this up on a network by the principle of \*\*\*\*\* using the liquid which dissolved or distributed fiber or the particle, and the binder. be involved in these fiber using comparatively long fiber with a die length of about 25mm to a paper-making object using a staple fiber with a die length of about 10mm -- the felt and a nonwoven fabric are obtained by \*\*\*\*\*. moreover, a hook -- be needlelike, hook fiber and be involved -- \*\* should be involved with the felt, airstream, or a stream -- \*\* serves as a nonwoven fabric. In these textiles, when especially a carbon fiber is used, after carrying out nonwoven fabric processing according the textile fabrics and fire resistance-ized yarn which carbonized or graphitized the plain weave fabric using fire resistance-ized spun yarn to the needle punch method, the water jet punching method, etc., the mat nonwoven fabric by the paper-making method using the nonwoven fabric, the fire resistance-ized yarn, carbonization yarn, or graphitization yarn carbonized or graphitized etc. is used preferably. For example, it is a carbon cross made from the carbon paper TGP series by Toray Industries, Inc., SO series, and E-TEK etc. Moreover, conductive particles, such as carbon black, and conductive fiber, such as a carbon fiber, can also be added as an adjuvant for conductive improvement.

[0021] As eyes of these porosity electric conduction sheet 1, 10 - 220 g/m<sup>2</sup> is desirable, and is 20 - 120 g/m<sup>2</sup> more preferably. When the eyes of a porosity electric conduction sheet are less than 10g/m<sup>2</sup>, there is an inclination for the reinforcement of a porosity electric conduction sheet to become low. Moreover, it becomes difficult to form the inorganic conductivity matter layer 2 in a porosity electric conduction sheet front face. Furthermore, when it constructs on the polyelectrolyte film, a catalyst bed, and the time of unification of an electrode substrate and a cell, there is an inclination for an electrode substrate to become thin, for it to be buried in a catalyst bed and for the diffusion / transparency effectiveness to the direction of a field to become inadequate. On the other hand, when eyes exceeded 220 g/m<sup>2</sup> and it constructs on a cell, an electrode substrate becomes thick and resistance becomes large.

[0022] The inorganic conductivity matter layer 2 prepared by request reduces the amount of catalysts which becomes useless by suppressing a permeate lump of the catalyst to the inside of an electrode substrate, the front face of an electrode catalyst bed prepared further upwards is made smooth, it is for raising the proton conductivity between proton exchange film-electrode catalyst beds, and the single material of various graphite or carbonaceous, or a metal and semimetal are mentioned as the component, for example. When using the electrode of this invention for electrochemistry equipment, as inorganic conductivity matter, it is desirable to use carbon material from a corrosion resistance viewpoint. As such carbon material, carbon black, such as oil furnace black, acetylene black, thermal black, and channel black, is desirable from electronic conductivity and particle size. as oil furnace black -- the Cabot Corp. make -- Balkan Peninsula XC-72, the Balkan Peninsula P, black PARUZU 880, black PARUZU 1100, black PARUZU 1300, black PARUZU 2000, and legal one -- the KETCHIEN black EC by 400 and LION, and the Mitsubishi Chemical make -- #3150, #3250, etc. mention -- having -- as acetylene black -- DIN by DENKI KAGAKU KOGYO K.K. -- a turnip -- a rack etc. is mentioned. the point that the electric resistance of an inorganic conductivity matter layer becomes low also in the above-mentioned carbon material -- the Cabot Corp. make -- the KETCHIEN black EC by Balkan Peninsula XC-72 and LION, and DIN by DENKI KAGAKU KOGYO K.K. -- a turnip -- racks or such mixture are desirable. Moreover, although especially the structure of an inorganic conductivity matter layer is not limited, in order to make good electronic conduction nature, fuel diffusibility, and wastewater nature, it is an effective embodiment to have a vesicular structure. A front-face side is dense especially, and it is a still more desirable embodiment that a porosity sheet side considers as a rough \*\*\*\*\* unsymmetrical vesicular structure, in order to suppress a permeate lump of a catalyst. although especially the approach of making an inorganic conductivity matter layer an unsymmetrical vesicular structure is not limited -- for example, a porosity sheet side -- \*\* -- an unsymmetrical vesicular structure can be made to discover by preparing the inorganic high conductivity matter and preparing the low inorganic conductivity matter of \*\* by the front-face side Moreover, although mixed with a resin solution, an unsymmetrical vesicular structure can be made to discover also in the so-called wet solidifying method immersed in the poor solvent to the so-called resin in which it is hard to dissolve resin,



- after making the resin solution which maintains the structure of an inorganic conductivity matter layer substantially distribute the inorganic conductivity matter and applying these dispersion liquid to a porosity sheet. The dimension height of the inorganic conductivity matter can have and evaluate the specific surface area ( $\text{m}^2/\text{g}$ ) of the inorganic conductivity matter. namely, the direction of the inorganic conductivity matter with a low specific surface area -- more -- \*\* -- it is the inorganic high conductivity matter. Although especially the measuring method of the specific surface area of the inorganic conductivity matter is not limited, it can be searched for, for example with a nitrogen adsorption process. A nitrogen adsorption process is the technique of making the deaerated inorganic conductivity matter immersed in liquid nitrogen, measuring the nitrogen volume which stuck to the inorganic conductivity matter front face at the time of a balance, and computing specific surface area from this value. the specific surface area of the inorganic conductivity matter -- desirable --  $1\text{m}^2/\text{g}$ – $2000\text{m}^2/\text{g}$  -- it is  $10\text{m}^2/\text{g}$ – $1000\text{m}^2/\text{g}$  more preferably. If it exceeds the upper limit of said numerical range, manufacture of the inorganic conductivity matter will become difficult, if less than the minimum of said numerical range, it will become difficult to make surface roughness of an inorganic conductivity matter layer below into the upper limit of said numerical range, and specific surface area has that it is not desirable.

[0023] Moreover, when specific surface area of SA ( $\text{m}^2/\text{g}$ ) and the inorganic conductivity matter of a \*\*\*\* side is set to SB ( $\text{m}^2/\text{g}$ ) for the specific surface area of the inorganic conductivity matter of a side dense [ the inorganic conductivity matter layer 2 of a front-face side is dense, and ] when a porosity sheet side is a rough \*\*\*\*\* unsymmetrical vesicular structure, these relation of  $1 < \text{SA}/\text{SB} \leq 2000$  and it being  $1.1 \leq \text{SA}/\text{SB} \leq 100$  more preferably is desirable. If SA/SB exceeds the upper limit of said numerical range here, the fuel diffusibility of the inorganic conductivity matter layer of a dense side worsens, it is not desirable and that SA/SB is less than the lower limit of said numerical range means that an inorganic conductivity matter layer does not serve as an unsymmetrical vesicular structure substantially.

[0024] As mentioned above, this invention as an electrode substrate 5 By the way, electronic conduction nature, It aims [ therefore ] at controlling a permeate lump of the catalyst to the inside of this base material that poses a problem as much as possible, in case the porosity electric conduction sheet 1 which is excellent in fuel diffusibility and wastewater nature is used. As the electrode catalyst bed 3 side front face 5 of an electrode substrate, i.e., an electrode substrate In adopting the thing of the mode which forms the inorganic conductivity matter layer 2 in one side of the electrode substrate 1 explained by drawing 1 or drawing 2 , the electrode catalyst bed 3 side front face of the minerals conductive material layer 2 moreover, the voice which forms the direct electrode catalyst bed 3 in the front face of the porosity electric conduction sheet 1 -- when adopting a thing [ like ], it is characterized by setting surface roughness of the electrode catalyst bed 3 side front face of the electrode catalyst bed 1 to 2 micrometers or more 20 micrometers or less. If there is an inclination for the fuel diffusibility of an electrode substrate to worsen if the surface roughness of an electrode substrate is less than 2 micrometers and 20 micrometers is exceeded, a permeate lump of the catalyst to an electrode substrate increases, and it is not desirable. From such a thing, more desirable surface roughness is 3 micrometers or more 15 micrometers or less. If it is made this surface roughness, fuel diffusibility and the catalyst \*\*\*\* lump inhibition nature to an electrode substrate will improve further.

[0025] Here, the surface roughness said by this invention is defined as the center line average of roughness height (Ra) among the specification of surface roughness which specifies by JIS B0601. This center line average of roughness height (Ra) expresses with the micrometer (micrometer) the value calculated by the following formula, when the direction of the X-axis and longitudinal magnification is expressed with a Y-axis and it expresses a granularity curve with  $y=f(x)$  for the center line of this sampling part by sampling the part of measurement die-length l in the direction of that center line from a granularity curve.

[0026]

[Equation 1]

$$R_a = \frac{1}{l} \int_0^l |f(x)| dx$$

[0027] Although especially limitation will not be carried out if the equipment which measures above-mentioned center line average-of-roughness-height  $R_a$  is the surface roughness measuring instrument which can perform measurement according to JIS B0601, a super-[ by KEYENCE CORP. ] depth surface type-like measuring microscope (format :VK- 8500) and Kosaka Laboratory Tabulation Side granularity measuring instrument (format :SE- 3300) can be used, for example.

[0028] Moreover, as for the gestalt of the inorganic conductivity matter, it is desirable that it is a particle-like. It is because there is an inclination to be hard coming to set up the surface roughness which the inorganic conductivity matter layer 2 mentioned above as they are gestalten other than the shape of a particle below to the upper limit of said numerical range. As this particle size, 10nm - 20 micrometers are 20nm - 100nm more preferably. If particle size is less than the lower limit of said numerical range, manufacture of the inorganic conductivity matter will become difficult, and on the other hand, when it exceeds the upper limit of said numerical range, there is an inclination it to become difficult to make surface roughness of an inorganic conductivity matter layer below into the upper limit of said numerical range.

[0029] Next, the example of 1 embodiment of the manufacture approach of the electrode substrate of this invention is explained.

[0030] First, a plain weave fabric is created using fire resistance-ized spun yarn, and carbon fiber textiles are created by carbonizing this plain weave fabric. This is equivalent to drawing 1 and the porosity electric conduction sheet 1 in 2. Next, the dispersion liquid of the inorganic conductivity matter are applied on carbon fiber textiles, and an inorganic conductivity matter layer is formed. This is equivalent to drawing 1 and the inorganic conductivity matter layer 2 in 2. By pressing or grinding this inorganic conductivity matter layer, it is JIS about surface roughness. It is made 2 micrometers or more 20 micrometers or less by the center line average of roughness height ( $R_a$ ) in B0601. Next, electrode catalyst dispersion liquid are applied on an inorganic conductivity matter layer, and an electrode catalyst bed is created. This is equivalent to the electrode catalyst bed 3 in drawing 2.

[0031] It is also desirable to apply and manufacture dispersion liquid on a sheet front face as an approach of carrying out the laminating of the inorganic conductivity matter to a porosity electric conduction sheet, and it is still more desirable as viscosity of inorganic conductivity matter dispersion liquid that they are more than 20Pa and s more preferably 10 or more Pa-s. When the viscosity of inorganic conductivity matter dispersion liquid is less than 10 Pa-s, and it applies to a porosity electric conduction sheet, there is an inclination it to become difficult for the inorganic conductivity matter to permeate in a sheet, to become easy to be crowded, and to prepare an inorganic conductivity matter layer in a porosity electric conduction sheet front face. A surfactant can also be added in inorganic conductivity matter dispersion liquid. By adding a surfactant, the effectiveness which the inorganic conductivity matter concordance-comes to be easy to dispersion liquid, and dispersion liquid stabilize is acquired. Moreover, when it is effective in lowering the viscosity of inorganic conductivity matter dispersion liquid, namely, the inorganic conductivity matter dispersion liquid of the same viscosity also add a surfactant, concentration of the inorganic conductivity matter can be made high more.

[0032] The viscosity of inorganic conductivity matter dispersion liquid is JIS K5400. It can measure according to Coating commercial-test approach 4.5.3 the "rotational-viscometer method" to specify. Although especially the equipment that measures viscosity is not limited, Brookfield viscometer [ by Tokyo Keiki Co., Ltd. ] B8L can be used, for example.

[0033] Although not limited especially as the manufacture approach of the electrode substrate in this invention, after forming the inorganic conductivity matter layer 2 in porosity electric

conduction sheet 1 front face, it is also a desirable embodiment to press and manufacture a front face. Although not limited especially as the approach of a press, a roll press, a monotonous press, etc. can be used. Moreover, heating is also a desirable embodiment in order to raise press effectiveness. As a pressure of a press, it is more preferably desirable that it is [ 1 or more MPas ] 5 or less MPa 0.1 or more-MPa 10 or less MPa. If a permeate lump of the electrode catalyst bed coating liquid which will be prepared in the front face of an inorganic conductivity matter layer if a pressure is less than the lower limit of said numerical range increases and it exceeds the upper limit of said numerical range preferably, the fuel diffusibility of an inorganic conductivity matter layer worsens and is not desirable. If it is the temperature which is easy to deform an inorganic conductivity matter layer as temperature of a press, it will not be limited especially. Moreover, the temperature which is easy to deform an inorganic conductivity matter layer Although it is hard to \*\*\*\*\* generally depending on the matter which constitutes an inorganic conductivity matter layer, when PTFE is contained in an inorganic conductivity matter layer, for example 327 degrees C or more when 350 degrees C or more 390 degrees C or less are more preferably desirable and 400 degrees C or less of tetrafluoroethylene-perfluoro vinyl ether copolymers (PFA) are contained 310 degrees C or more 400 degrees C or less, 330 degrees C or more 390 degrees C or less are more preferably desirable, and when a tetrafluoroethylene-6 fluoride propylene copolymer (FEP) is contained, 270 degrees C or more 300 degrees C or less are more preferably desirable 250 degrees C or more 320 degrees C or less. If press temperature is less than the lower limit of said numerical range, it will be hard coming to deform an inorganic conductivity matter layer, and preferably, when it exceeds the upper limit of said numerical range, there is an inclination the fluorine compound in an inorganic conductivity matter layer becomes easy to decompose. When a surfactant is contained in the inorganic conductivity matter layer 2, it is an embodiment desirable when heating even to the decomposition temperature of a surfactant, performing preliminary baking, and also making a surfactant disassemble in front of a press raises the fuel permeability of an inorganic conductivity matter layer.

[0034] Furthermore, after preparing an inorganic conductivity matter layer in a porosity electric conduction sheet front face, it is also a desirable embodiment to grind and manufacture a front face. Although not limited especially as a polish base material, abrasive cloth, abrasive paper, an abrasive belt, a polish sheet, an abrasive disc, a brush roll, etc. can be used. Moreover, although not limited especially as abrasives, an alumina, a zirconia, a fused alumina, silicon carbide, a garnet, emery, etc. can be used.

[0035] Drawing 1 , the electrode substrate which consists of a porosity electric conduction sheet of this invention of 2 or this electrode substrate, and an electrode catalyst bed and the film-electrode complex (MEA) which consists of solid-electrolyte membranes of drawing 3 can be adapted for various electrochemistry equipments. Inside, water electrolysis equipment and a fuel cell are desirable, and still more suitable for a polymer electrolyte fuel cell or a direct methanol mold fuel cell also in a fuel cell.

[0036] Furthermore, although it thinks especially as an application of the fuel cell using the electrode substrate of this invention, without being limited, in a polymer electrolyte fuel cell, the power source of supply of the mobile which is a useful application is desirable. It is a mobile with automobiles, such as a passenger car, a bus, and a truck, especially desirable a vessel, a railroad, etc. In a direct methanol mold fuel cell, the power source of supply of the pocket electronic equipment which is a useful application is also still more desirable. It is pocket electronic equipment with a cellular phone, especially desirable a computer, a navigation system, etc.

[0037]

[Example] Hereafter, although drawing 1 thru/or drawing 3 , an example, and the example of a comparison explain this invention to a detail, this invention is not limited to these. moreover, the following examples and examples of a comparison -- setting -- viscosity -- all -- Brookfield viscometer [ by Tokyo Keiki Co., Ltd. ] B8L -- using -- the temperature of 25 degrees C -- setting -- measurement -- carrying out -- surface roughness -- all -- the shape of super-[ by KEYENCE CORP. ] depth surface type -- it measured using measuring microscope VK-8500.

[0038] As an inorganic conductivity matter layer 2 of creation drawing 1 of example 1(1)

inorganic conductivity matter dispersion liquid, in order to obtain the inorganic conductivity matter, 12g [ of surfactants ] (it purchases from TRITON X-114 and Nakarai Tesuku, Inc.) and acetylene black (DENKA BLACK, DENKI KAGAKU KOGYO K.K. make, and nitrogen specific-surface-area 61m<sup>2</sup>/g) 6g, 2.5g (made in [ Daikin Industries, LTD. ] Pori Flon PTFE) of PTFE water dispersions, and 39.5g of water were mixed, and it fully agitated with the homogenizer. The viscosity of the obtained dispersion liquid was 800 Pa-s.

[0039] (2) It sank into carbon fiber textiles (the cross made from E-TEK, Type A, superintendent officer 116 g/m<sup>2</sup>), and they were made to dry a PTFE water dispersion (made in [ Daikin Industries, LTD. ] Pori Flon PTFE) as creation of an electrode substrate, and a porosity electric conduction sheet 1. The PTFE content of the obtained textiles was 20wt(s)%. On one side of these textiles The dispersion liquid created by (1) were applied and it was made to dry at 100 degrees C immediately. 2mg /of amounts with acetylene black of the obtained textiles was [ cm ] 2. The press which puts the pressure of 380 degrees C and 3MPa on these textiles, and is covered for 15 minutes, with the pressure of 3MPa maintained and which is cooled to a room temperature was performed, and the electrode substrate was obtained. The surface roughness of the side (smooth side) to which the inorganic conductivity matter of the obtained electrode substrate has adhered was 9 micrometers.

[0040] (3) In the Nafion solution made from creation Aldrich of an electrode substrate with an electrode catalyst bed, in addition, catalyst support carbon (catalyst :P. t, ValcanXCmade from carbon:Cabot- 72, the amount of platinum support : 50 % of the weight) was well agitated so that the weight ratio of platinum and Nafion might be set to 1:0.5, and the catalyst-polymer constituent was prepared in it. This catalyst-polymer constituent was applied to the smooth electrode substrate side created by (2), was dried immediately, and the electrode substrate 5 with an electrode catalyst bed was created. The electrode catalyst bed of the obtained electrode substrate with an electrode catalyst bed was coating weight 0.5 mg/cm<sup>2</sup> of platinum.

[0041] (4) As a film-electrode zygote of creation of a film-electrode zygote, and evaluation drawing 3 , between the electrode substrates with an electrode catalyst bed of two sheets created above (3), the proton exchange film (Nafion112 made from DuPont) was inserted so that an electrode catalyst bed might touch the proton exchange film, it carried out the hotpress on condition that 130 degrees C and 5MPa, and was used as the zygote. The obtained zygote was built into the fuel cell cel, the hydrogen and air of ordinary pressure (atmospheric pressure) were supplied, and the current-electrical-potential-difference (I-V) property was measured on conditions with an operating temperature of 70 degrees C. Horsepower outputs are 450 mW/cm<sup>2</sup> and showed the outstanding high power property.

[0042] The PTFE water dispersion (made in [ Daikin Industries, LTD. ] Pori Flon PTFE) was calcinated at 380 degrees C after sinking in and desiccation on the creation carbon fiber textiles (the cross made from E-TEK, Type A, superintendent officer 116 g/m<sup>2</sup>) of the example 1 (1) electrode substrate of a comparison. The PTFE content of the obtained electrode substrate was 20wt(s)%, and surface roughness was 30 micrometers.

[0043] (2) The catalyst-polymer constituent was applied to one side of the electrode substrate created by the creation above (1) of an electrode substrate with an electrode catalyst bed like the example 1 (3), it dried immediately, and the electrode substrate with an electrode catalyst bed was created. The electrode catalyst bed of the obtained electrode substrate with an electrode catalyst bed was coating weight 0.5 mg/cm<sup>2</sup> of platinum.

[0044] (3) Using the electrode substrate with an electrode catalyst bed created by creation and the evaluation above (2) of a film-electrode zygote, the film-electrode zygote was created like the example 1 (4), and the I-V property was measured. The horsepower outputs were 100 mW/cm<sup>2</sup> and were the output characteristics inferior to an example 1. The surface roughness of an electrode substrate is coarse compared with an example 1, and it thinks because an electrode catalyst bed was not able to form a good junction interface between penetration, the proton exchange film, and an electrode catalyst at an electrode substrate.

[0045] It sank into the creation carbon fiber textiles (the cross made from E-TEK, Type A, superintendent officer 116 g/m<sup>2</sup>) of the example 2 (1) electrode substrate of a comparison, and they were made to dry a PTFE water dispersion (made in [ Daikin Industries, LTD. ] Pori Flon

PTFE). The PTFE content of the obtained textiles was 20wt(s)%. The dispersion liquid created in the example 1 (1) were applied to one side of these textiles, and it was made to dry at 100 degrees C immediately. These textiles were calcinated at 380 degrees C. The amount with acetylene black of the obtained textiles was 2 mg/cm<sup>2</sup>, and the surface roughness of the side to which the inorganic conductivity matter has adhered was 25 micrometers.

[0046] (2) The catalyst-polymer constituent was applied to the side to which the inorganic conductivity matter of the electrode substrate created by the creation above (1) of an electrode substrate with an electrode catalyst bed has adhered like the example 1 (3), it dried immediately, and the electrode substrate with an electrode catalyst bed was created. The electrode catalyst bed of the obtained electrode substrate with an electrode catalyst bed was coating weight 0.5 mg/cm<sup>2</sup> of platinum.

[0047] (3) Using the electrode substrate with an electrode catalyst bed created by creation and the evaluation above (2) of a film-electrode zygote, the film-electrode zygote was created like the example 1 (4), and the I-V property was measured. The horsepower outputs were 200 mW/cm<sup>2</sup> and were the output characteristics inferior to an example 1. The surface roughness of an electrode substrate is coarse compared with an example 1, and it thinks because an electrode catalyst bed was not able to form a good junction interface between penetration, the proton exchange film, and an electrode catalyst at an electrode substrate.

[0048] It sank into the creation carbon fiber textiles (the cross made from E-TEK, Type A, superintendent officer 116 g/m<sup>2</sup>) of the example 3 (1) electrode substrate of a comparison, and they were made to dry a PTFE water dispersion (made in [ Daikin Industries, LTD. ] Pori Flon PTFE). The PTFE content of the obtained textiles was 20wt(s)%. The dispersion liquid created in the example 1 (1) were applied to one side of these textiles, and it was made to dry at 100 degrees C immediately. 5mg /of amounts with acetylene black of the obtained textiles was [ cm ] 2. The press which puts the pressure of 380 degrees C and 100MPa on these textiles, and is covered for 15 minutes, with the pressure of 100MPa maintained and which is cooled to a room temperature was performed, and the electrode substrate was obtained. The surface roughness of the side (smooth side) to which the inorganic conductivity matter of the obtained electrode substrate has adhered was 1 micrometer.

[0049] (2) The catalyst-polymer constituent was applied to one side of the electrode substrate created by the creation above (1) of an electrode substrate with an electrode catalyst bed like the example 1 (3), it dried immediately, and the electrode substrate with an electrode catalyst bed was created. The electrode catalyst bed of the obtained electrode substrate with an electrode catalyst bed was coating weight 0.5 mg/cm<sup>2</sup> of platinum.

[0050] (3) Using the electrode substrate with an electrode catalyst bed created by creation and the evaluation above (2) of a film-electrode zygote, the film-electrode zygote was created like the example 1 (4), and the I-V property was measured. The horsepower outputs were 100 mW/cm<sup>2</sup> and were the output characteristics inferior to an example 1. The surface roughness of an electrode substrate is fine compared with an example 1, and it thinks because generation water was stuck for the electrode substrate and gaseous diffusion nature worsened.

[0051] 0.5g [ of creation surfactants of example of comparison 4(1) inorganic conductivity matter dispersion liquid ] (it purchases from TRITON X-114 and Nakarai Tesuku, Inc.) and acetylene black (DENKA BLACK, DENKI KAGAKU KOGYO K.K. make, particle size of 42nm) 2g, 0.83g (made in [ Daikin Industries, LTD. ] Pori Flon PTFE) of PTFE water dispersions, and 12.9g of water were mixed, and it fully agitated with the homogenizer. The viscosity of the obtained dispersion liquid was 1 Pa-s.

[0052] (2) It sank into the creation carbon fiber textiles (the cross made from E-TEK, Type A, superintendent officer 116 g/m<sup>2</sup>) of an electrode substrate, and they were made to dry a PTFE water dispersion (made in [ Daikin Industries, LTD. ] Pori Flon PTFE). The PTFE content of the obtained textiles was 20wt(s)%. The dispersion liquid created by (1) were applied to one side of these textiles, and it was made to dry at 100 degrees C immediately. 2mg /of amounts with acetylene black of the obtained textiles was [ cm ] 2. The press which puts the pressure of 380 degrees C and 3MPa on these textiles, and is covered for 15 minutes, with the pressure of 3MPa maintained and which is cooled to a room temperature was performed, and the electrode

substrate was obtained. The surface roughness of the side to which the inorganic conductivity matter of the obtained electrode substrate has adhered was 25 micrometers.

[0053] (3) The catalyst-polymer constituent was applied to the side to which the inorganic conductivity matter of the electrode substrate created by the creation above (2) of an electrode substrate with an electrode catalyst bed has adhered like the example 1 (3), it dried immediately, and the electrode substrate with an electrode catalyst bed was created. The electrode catalyst bed of the obtained electrode substrate with an electrode catalyst bed was coating weight 0.5 mg/cm<sup>2</sup> of platinum.

[0054] (4) Using the electrode substrate with an electrode catalyst bed created by creation and the evaluation above (3) of a film-electrode zygote, the film-electrode zygote was created like the example 1 (4), and the I-V property was measured. The horsepower outputs were 200 mW/cm<sup>2</sup> and were the output characteristics inferior to an example 1. The viscosity of inorganic conductivity matter dispersion liquid is low compared with an example 1, and since the inorganic conductivity matter sank into textiles, the surface roughness of an electrode substrate becomes coarse compared with an example 1, and it thinks because an electrode catalyst bed was not able to form a good junction interface between penetration, the proton exchange film, and an electrode catalyst at an electrode substrate.

[0055] It sank into the creation carbon fiber textiles (the cross made from E-TEK, Type A, superintendent officer 116 g/m<sup>2</sup>) of an example 2 (1) electrode substrate, and they were made to dry a PTFE water dispersion (made in [ Daikin Industries, LTD. ] Pori Flon PTFE). The PTFE content of the obtained textiles was 20wt(s)%. The dispersion liquid created in the example 1 (1) were applied to one side of these textiles, and it was made to dry at 100 degrees C immediately. 2mg /of amounts with acetylene black of the obtained textiles was [ cm ] 2. 280-degree C oven performed desurfactant processing for these textiles over 2 hours. The press which puts the pressure of 380 degrees C and 3MPa on these textiles, and is covered for 15 minutes, with the pressure of 3MPa maintained and which is cooled to a room temperature was performed, and the electrode substrate was obtained. The surface roughness of the side (smooth side) to which the inorganic conductivity matter of the obtained electrode substrate has adhered was 9 micrometers.

[0056] (2) The catalyst-polymer constituent was applied to the side to which the inorganic conductivity matter of the electrode substrate created by the creation above (1) of an electrode substrate with an electrode catalyst bed has adhered like the example 1 (3), it dried immediately, and the electrode substrate with an electrode catalyst bed was created. The electrode catalyst bed of the obtained electrode substrate with an electrode catalyst bed was coating weight 0.5 mg/cm<sup>2</sup> of platinum.

[0057] (3) Using the electrode substrate with an electrode catalyst bed created by creation and the evaluation above (2) of a film-electrode zygote, the film-electrode zygote was created like the example 1 (4), and the I-V property was measured. Horsepower outputs are 450 mW/cm<sup>2</sup> and showed the outstanding high power property.

[0058] It sank into the creation carbon paper (the Toray Industries, Inc. make, TGP-H -060, superintendent officer 83 g/m<sup>2</sup>) of an example 3 (1) electrode substrate, and it was made to dry a PTFE water dispersion (made in [ Daikin Industries, LTD. ] Pori Flon PTFE). The PTFE content of the obtained carbon paper was 20wt(s)%. The dispersion liquid created in the example 1 (1) were applied to one side of this carbon paper, and it was made to dry at 100 degrees C immediately. The amount with acetylene black of the obtained carbon paper was 1 mg/cm<sup>2</sup>. The press which puts the pressure of 380 degrees C and 3MPa on this carbon paper, and is covered for 15 minutes, with the pressure of 3MPa maintained and which is cooled to a room temperature was performed, and the electrode substrate was obtained. The surface roughness of the side (smooth side) to which the inorganic conductivity matter of the obtained electrode substrate has adhered was 9 micrometers.

[0059] (2) The catalyst-polymer constituent was applied to the side to which the inorganic conductivity matter of the electrode substrate created by the creation above (1) of an electrode substrate with an electrode catalyst bed has adhered like the example 1 (3), it dried immediately, and the electrode substrate with an electrode catalyst bed was created. The electrode catalyst

bed of the obtained electrode substrate with an electrode catalyst bed was coating weight 0.5 mg/cm<sup>2</sup> of platinum.

[0060] (3) Using the electrode substrate with an electrode catalyst bed created by creation and the evaluation above (2) of a film-electrode zygote, the film-electrode zygote was created like the example 1 (4), and the I-V property was measured. Horsepower outputs are 450 mW/cm<sup>2</sup> and showed the outstanding high power property.

[0061] The PTFE water dispersion (made in [ Daikin Industries, LTD. ] Pori Flon PTFE) was calcinated at 380 degrees C after sinking in and desiccation to the creation carbon paper (the Toray Industries, Inc. make, TGP-H -060, superintendent officer 83 g/m<sup>2</sup>) of the example 5 (1) electrode substrate of a comparison. The PTFE content of the obtained electrode substrate was 20wt(s)%, and surface roughness was 21 micrometers.

[0062] (2) The catalyst-polymer constituent was applied to one side of the electrode substrate created by the creation above (1) of an electrode substrate with an electrode catalyst bed like the example 1 (3), it dried at 100 degrees C immediately, and the electrode substrate with an electrode catalyst bed was created. The electrode catalyst bed of the obtained electrode substrate with an electrode catalyst bed was coating weight 0.5 mg/cm<sup>2</sup> of platinum.

[0063] (3) Using the electrode substrate with an electrode catalyst bed created by creation and the evaluation above (2) of a film-electrode zygote, the film-electrode zygote was created like the example 1 (4), and the I-V property was measured. The horsepower outputs were 350 mW/cm<sup>2</sup> and were the output characteristics inferior to an example 3. The surface roughness of an electrode substrate is coarse compared with an example 3, and it thinks because an electrode catalyst bed was not able to form a good junction interface between penetration, the proton exchange film, and an electrode catalyst at an electrode substrate.

[0064] The staple fiber of the PAN system carbon fiber (diameter of 7 micrometers) cut into creation die length of 12mm of the example 6 (1) electrode substrate of a comparison was underwater milled on distribution and a wire gauze, and the emulsion which consists of mixture of the polyvinyl alcohol which is the polymeric material which binds a carbon staple fiber, and vinyl acetate was made to adhere, it dried, and the porosity electric conduction sheet which consists of carbon fiber paper was obtained. This carbon fiber paper was calcinated and the carbon paper of eyes 5 g/m<sup>2</sup> was obtained. It sank into this carbon paper and it was made to dry a PTFE water dispersion (made in [ Daikin Industries, LTD. ] Pori Flon PTFE). The PTFE content of the obtained porosity electric conduction sheet was 20wt(s)%. Although it was going to apply to one side of this porosity electric conduction sheet the dispersion liquid created in the example 1 (1), it could not apply well and an inorganic conductivity matter layer was not able to be formed. Since the superintendent officer of a porosity electric conduction sheet was too low, it thinks.

[0065] 12g [ of creation surfactants of inorganic conductivity matter dispersion liquid with a small example 4 (1) specific surface area ] (it purchases from TRITON X-114 and Nakarai Tesuku, Inc.) and acetylene black (DENKA BLACK, DENKI KAGAKU KOGYO K.K. make, and nitrogen specific-surface-area 61m<sup>2</sup>/g) 6g, 2.5g (made in [ Daikin Industries, LTD. ] Pori Flon PTFE) of PTFE water dispersions, and 39.5g of water were mixed, and it fully agitated with the homogenizer. The viscosity of the obtained dispersion liquid was 800 Pa-s.

[0066] (2) 12g [ of creation surfactants of inorganic conductivity matter dispersion liquid with a large specific surface area ] (it purchases from TRITON X-114 and Nakarai Tesuku, Inc.) and oil furnace black (ValcanXC-72, product [ made from Cabot ], and nitrogen specific-surface-area 254m<sup>2</sup>/g) 6g and 2.5g (made in [ Daikin Industries, LTD. ] Pori Flon PTFE) of PTFE water dispersions were mixed, and it fully agitated with the homogenizer. Water was added and adjusted so that the viscosity of the obtained dispersion liquid might serve as 100 Pa-s.

[0067] (3) The front-face side of the inorganic conductivity matter applied inorganic conductivity matter dispersion liquid with a small specific surface area created by (1) to one side of the electrode substrate created by the example of creation comparison 1 above (1) of the electrode substrate formed in dense unsymmetrical structure, and made it dry at 100 degrees C immediately. 1mg /of amounts with acetylene black of the obtained textiles was [ cm ] 2. Inorganic conductivity matter dispersion liquid with a large specific surface area moreover further created by (2) were applied, and it was made to dry at 100 degrees C immediately.

1mg /of amounts with oil furnace black of the obtained textiles was [ cm ] 2. Thus, the front-face side of the inorganic conductivity matter obtained the electrode substrate formed in dense unsymmetrical structure. The surface roughness of the side (smooth side) to which the inorganic conductivity matter of the obtained electrode substrate has adhered was 10 micrometers.

[0068] (4) The catalyst-polymer constituent was applied to the side to which the inorganic conductivity matter of the electrode substrate created by the creation above (3) of an electrode substrate with an electrode catalyst bed has adhered like the example 1 (3), it dried immediately, and the electrode substrate with an electrode catalyst bed was created. The electrode catalyst bed of the obtained electrode substrate with an electrode catalyst bed was coating weight 0.5 mg/cm<sup>2</sup> of platinum.

[0069] (5) Using the electrode substrate with an electrode catalyst bed created by creation and the evaluation above (4) of a film-electrode zygote, the film-electrode zygote was created like the example 1 (4), and the I-V property was measured. Horsepower outputs are 450 mW/cm<sup>2</sup> and showed the outstanding high power property.

[0070] 12g [ of creation surfactants of inorganic conductivity matter dispersion liquid with a small example 5 (1) specific surface area ] (it purchases from TRITON X-114 and Nakarai Tesuku, Inc.) and acetylene black (DENKA BLACK, DENKI KAGAKU KOGYO K.K. make, and nitrogen specific-surface-area 61m<sup>2</sup>/g) 6g, 2.5g (made in [ Daikin Industries, LTD. ] Pori Flon PTFE) of PTFE water dispersions, and 39.5g of water were mixed, and it fully agitated with the homogenizer. The viscosity of the obtained dispersion liquid was 800 Pa-s.

[0071] (2) 12g [ of creation surfactants of inorganic conductivity matter dispersion liquid with a large specific surface area ] (it purchases from TRITON X-114 and Nakarai Tesuku, Inc.) and oil furnace black (KETCHIEN black EC, LION make, and nitrogen specific-surface-area 1000m<sup>2</sup>/g) 6g and 2.5g (made in [ Daikin Industries, LTD. ] Pori Flon PTFE) of PTFE water dispersions were mixed, and it fully agitated with the homogenizer. Water was added and adjusted so that the viscosity of the obtained dispersion liquid might serve as 100 Pa-s.

[0072] (3) The front-face side of the inorganic conductivity matter applied inorganic conductivity matter dispersion liquid with a small specific surface area created by (1) to one side of the electrode substrate created by the example of creation comparison 1 above (1) of the electrode substrate formed in dense unsymmetrical structure, and made it dry at 100 degrees C immediately. 1mg /of amounts with acetylene black of the obtained textiles was [ cm ] 2.

Inorganic conductivity matter dispersion liquid with a large specific surface area moreover further created by (2) were applied, and it was made to dry at 100 degrees C immediately. 1mg /of amounts with oil furnace black of the obtained textiles was [ cm ] 2. Thus, the front-face side of the inorganic conductivity matter obtained the electrode substrate formed in dense unsymmetrical structure. The surface roughness of the side (smooth side) to which the inorganic conductivity matter of the obtained electrode substrate has adhered was 10 micrometers.

[0073] (4) The catalyst-polymer constituent was applied to the side to which the inorganic conductivity matter of the electrode substrate created by creation (3) of an electrode substrate with an electrode catalyst bed has adhered like the example 1 (3), it dried immediately, and the electrode substrate with an electrode catalyst bed was created. The electrode catalyst bed of the obtained electrode substrate with an electrode catalyst bed was coating weight 0.5 mg/cm<sup>2</sup> of platinum.

(5) Using the electrode substrate with an electrode catalyst bed created by creation and evaluation (4) of a film-electrode zygote, the film-electrode zygote was created like the example 1 (4), and the I-V property was measured. Horsepower outputs are 450 mW/cm<sup>2</sup> and showed the outstanding high power property.

[0074] The near front face to which the inorganic conductivity matter of the electrode substrate created in the example 2 of a creation comparison (1) of an example 6 (1) electrode substrate has adhered was ground by sand paper (No. 1000). The surface roughness of the side to which the inorganic conductivity matter of the obtained electrode substrate has adhered was 10 micrometers.

[0075] (2) The catalyst-polymer constituent was applied to the side to which the inorganic conductivity matter of the electrode substrate created by the creation above (1) of an electrode



substrate with an electrode catalyst bed has adhered like the example 1 (3), it dried immediately, and the electrode substrate with an electrode catalyst bed was created. The electrode catalyst bed of the obtained electrode substrate with an electrode catalyst bed was coating weight 0.5 mg/cm<sup>2</sup> of platinum.

[0076] (3) Using the electrode substrate with an electrode catalyst bed created by creation and the evaluation above (2) of a film-electrode zygote, the film-electrode zygote was created like the example 1 (4), and the I-V property was measured. Horsepower outputs are 450 mW/cm<sup>2</sup> and showed the outstanding high power property.

[0077] In the Nafion solution made from creation Aldrich of the electrode substrate with an electrode catalyst bed which has an example 7 (1) vesicular structure, in addition, catalyst support carbon (catalyst :P. t, ValcanXCmade from carbon:Cabot- 72, the amount of platinum support : 50 % of the weight) was well agitated so that the weight ratio of platinum and Nafion might be set to 1:0.5, and the catalyst-polymer constituent was prepared in it. This catalyst-polymer constituent was applied to the smooth electrode substrate side created by the example 1 (1) and (2), it was immediately immersed in butyl acetate, and the electrode substrate to which the electrode catalyst bed which has a three-dimensions mesh vesicular structure was attached was created. The electrode catalyst bed of the obtained electrode substrate with an electrode catalyst bed was coating weight 0.5 mg/cm<sup>2</sup> of platinum.

[0078] (2) Using the electrode substrate with an electrode catalyst bed created by creation and the evaluation above (1) of a film-electrode zygote, the film-electrode zygote was created like the example 1 (4), and the I-V property was measured. Horsepower outputs are 500 mW/cm<sup>2</sup> and showed the outstanding high power property.

[0079] In the Nafion solution made from creation Aldrich of an electrode substrate with an example 8(1) electrode catalyst bed, in addition, catalyst support carbon (the amount of ruthenium [ the KETCHIEN black EC by catalyst-t and Ru, and carbon:LION, amount:of platinum support 30 % of the weight, and ] support: 24 % of the weight) was well agitated so that the weight ratio of carbon and Nafion might be set to 1:0.5, and the catalyst-polymer constituent was prepared in it. This catalyst-polymer constituent was applied to the smooth electrode substrate side created in the example 1 (2), was dried immediately, and the electrode substrate with an electrode catalyst bed was created. The electrode catalyst bed of the obtained electrode substrate with an electrode catalyst bed was coating weight 1.0 mg/cm<sup>2</sup> of platinum.

[0080] (2) Between the electrode substrates with an electrode catalyst bed created in the electrode substrate with an electrode catalyst bed and example 1 (3) which were created by creation and the evaluation above (1) of a film-electrode zygote, the proton exchange film (Nafion112 made from DuPont) was inserted so that an electrode catalyst bed might touch the proton exchange film, it carried out the hotpress on condition that 130 degrees C and 5MPa, and was used as the zygote. The obtained zygote was built into the fuel cell cel, the 50mol% methanol water solution and air of ordinary pressure (atmospheric pressure) were supplied, and the current-electrical-potential-difference (I-V) property was measured on conditions with an operating temperature of 25 degrees C. Horsepower outputs are 50 mW/cm<sup>2</sup> and showed the outstanding high power property.

[0081] In the Nafion solution made from creation Aldrich of an electrode substrate with an example of comparison 7(1) electrode catalyst bed, in addition, catalyst support carbon (the amount of ruthenium [ the KETCHIEN black EC by catalyst-t and Ru, and carbon:LION, amount:of platinum support 30 % of the weight, and ] support: 24 % of the weight) was well agitated so that the weight ratio of carbon and Nafion might be set to 1:0.5, and the catalyst-polymer constituent was prepared in it. This catalyst-polymer constituent was applied to the side to which the inorganic conductivity matter of the electrode substrate created in the example 2 of a comparison (1) has adhered, was dried immediately, and the electrode substrate with an electrode catalyst bed was created. The electrode catalyst bed of the obtained electrode substrate with an electrode catalyst bed was coating weight 1.0 mg/cm<sup>2</sup> of platinum.

[0082] (2) Using the electrode substrate with an electrode catalyst bed created in the electrode substrate with an electrode catalyst bed and the example 2 of a comparison (2) which were created by creation and the evaluation above (1) of a film-electrode zygote, the film-electrode

zygote was created like the example 7 (2), and the I-V property was measured. The horsepower outputs were 20 mW/cm<sup>2</sup> and were the output characteristics inferior to an example 8. The surface roughness of an electrode substrate is coarse compared with an example 8, and it thinks because an electrode catalyst bed was not able to form a good junction interface between penetration, the proton exchange film, and an electrode catalyst at an electrode substrate.

[0083] 12g [ of creation surfactants of example 9(1) inorganic conductivity matter dispersion liquid ] (it purchases from TRITON X-114 and Nakarai Tesuku, Inc.) and acetylene black (DENKA BLACK, DENKI KAGAKU KOGYO K.K. make, and nitrogen specific-surface-area 61m<sup>2</sup>/g) 6g, 2.5g (made in [ Daikin Industries, LTD. ] Pori Flon PTFE) of PTFE water dispersions, and 39.5g of water were mixed, and it fully agitated with the homogenizer. In order to raise the viscosity of dispersion liquid, it heated to 60 degrees C during stirring, and a part of moisture was evaporated. The viscosity of the obtained dispersion liquid was 1600 Pa-s.

[0084] (2) The dispersion liquid created by (1) were applied to one side of the creation carbon fiber textiles (the cross made from E-TEK, Type A, superintendent officer 116 g/m<sup>2</sup>) of an electrode substrate, and it was made to dry at 100 degrees C immediately. 2mg /of amounts with acetylene black of the obtained textiles was [ cm ] 2. The press which puts the pressure of 380 degrees C and 3MPa on these textiles, and is covered for 15 minutes, with the pressure of 3MPa maintained and which is cooled to a room temperature was performed, and the electrode substrate was obtained. The surface roughness of the side (smooth side) to which the inorganic conductivity matter of the obtained electrode substrate has adhered was 9 micrometers.

[0085] (3) The catalyst-polymer constituent was applied to the side to which the inorganic conductivity matter of the electrode substrate created by the creation above (2) of an electrode substrate with an electrode catalyst bed has adhered like the example 1 (3), it dried immediately, and the electrode substrate with an electrode catalyst bed was created. The electrode catalyst bed of the obtained electrode substrate with an electrode catalyst bed was coating weight 0.5 mg/cm<sup>2</sup> of platinum.

[0086] (4) Using the electrode substrate with an electrode catalyst bed created by creation and the evaluation above (3) of a film-electrode zygote, the film-electrode zygote was created like the example 1 (4), and the I-V property was measured. Horsepower outputs are 450 mW/cm<sup>2</sup> and showed the outstanding high power property.

[0087]

[Effect of the Invention] By this invention, compared with the conventional thing, fuel diffusibility and wastewater nature can be good, can suppress a permeate lump of a catalyst bed, and can offer a highly efficient electrode substrate with the still higher proton conductivity between a catalyst bed and the proton exchange film, and its manufacture approach.

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[Translation done.]

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is drawing of longitudinal section of one example of the electrode substrate of this invention.

[Drawing 2] The electrode substrate of drawing 1 is drawing of longitudinal section of the electrode substrate of this invention of a different mode.

[Drawing 3] The electrode substrate of drawing 2 is drawing of longitudinal section of the electrode substrate of this invention of a different mode.

[Description of Notations]

- 1 .... Porosity electric conduction sheet
- 2 .... Minerals conductivity matter layer
- 3 .... Electrode catalyst bed
- 4 .... Proton exchange film
- 5 .... Electrode substrate (this invention)

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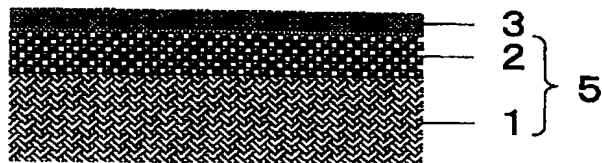
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(54) 【発明の名称】 電極基材およびその製造方法並びにそれを用いた燃料電池

(57) 【要約】

【課題】 従来のものに比べて燃料拡散性、排水性がよく、触媒層の浸み込みを抑えることができる高性能な電極基材5およびその製造方法を提供すること。

【解決手段】 無機導電性繊維からなる多孔質導電性シート1を含む電極基材5において、該シート1の電極触媒層を設ける側の表面粗さを、J I S B 0 6 0 1で規定する表面粗さ (Ra) で2  $\mu$  m以上20  $\mu$  m以下にする。



## 【特許請求の範囲】

【請求項 1】 無機導電性繊維からなる多孔質の導電シートを含む電極基材において、該シートの電極触媒層を設ける側の表面粗さが、JIS B0601で規定する中心線平均粗さ (Ra) で  $2\mu\text{m}$  以上  $20\mu\text{m}$  以下であることを特徴とする電極基材。

【請求項 2】 多孔質導電シートの表面に、さらに無機導電性物質層が設けられていることを特徴とする請求項 1 記載の電極基材。

【請求項 3】 無機導電性物質が粒子状の形態を有することを特徴とする請求項 2 記載の電極基材。

【請求項 4】 無機導電性物質が炭素材であることを特徴とする請求項 2 または 3 に記載の電極基材。

【請求項 5】 炭素材がカーボンブラックであることを特徴とする請求項 4 記載の電極基材。

【請求項 6】 無機導電性物質層は、表面側が密であり、多孔質導電シート側が粗である非対称多孔質構造に形成されていることを特徴とする請求項 2～5 のいずれかに記載の電極基材。

【請求項 7】 無機導電性物質層は、表面側の無機導電性物質の比表面積を  $SA\text{ (m}^2/\text{g)}$ 、多孔質導電シート側の無機導電性物質の比表面積を  $SB\text{ (m}^2/\text{g)}$  とするとき、これらの関係が  $1 < SA/SB \leq 2000$  であることを特徴とする請求項 6 記載の電極基材。

【請求項 8】 多孔質導電シートが無機導電性繊維を用いたものであることを特徴とする請求項 1～7 のいずれかに記載の電極基材。

【請求項 9】 無機導電性繊維が炭素繊維であることを特徴とする請求項 8 記載の電極基材。

【請求項 10】 炭素繊維が、ポリアクリロニトリル、ピッチ、あるいは低沸点有機化合物を原料とするものであることを特徴とする請求項 9 記載の電極基材。

【請求項 11】 多孔質導電シートが、織布、抄紙体、フェルト、不織布のいずれかであることを特徴とする請求項 1～10 のいずれかに記載の電極基材。

【請求項 12】 多孔質導電シートの目付けが  $10\sim 220\text{ g/m}^2$  であることを特徴とする請求項 1～11 のいずれかに記載の電極基材。

【請求項 13】 多孔質導電シートの表面に、粘度が  $10\text{ Pa}\cdot\text{s}$  以上である無機導電性物質分散液を塗布することを特徴とする請求項 2 記載の電極基材の製造方法。

【請求項 14】 多孔質導電シートの表面に無機導電性物質層を設けた後、無機導電性物質層の表面をプレスまたは研磨することを特徴とする請求項 2 記載の電極基材の製造方法。

【請求項 15】 請求項 1～12 のいずれかに記載の電極基材を用いた膜-電極複合体。

【請求項 16】 請求項 1～12 のいずれかに記載の電極基材を用いた電気化学装置。

【請求項 17】 請求項 1～12 のいずれかに記載の電

極基材を用いた水電解装置。

【請求項 18】 請求項 1～12 のいずれかに記載の電極基材を用いた燃料電池。

【請求項 19】 請求項 1～12 のいずれかに記載の電極基材を用いた固体高分子型燃料電池。

【請求項 20】 請求項 1～12 のいずれかに記載の電極基材を用いた直接メタノール型燃料電池。

【請求項 21】 請求項 18～20 のいずれかに記載の燃料電池を電力供給源とする移動体。

【請求項 22】 請求項 18～20 のいずれかに記載の燃料電池を電力供給源とする自動車。

【請求項 23】 請求項 18～20 のいずれかに記載の燃料電池を電力供給源とする携帯電子機器。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】 本発明は、燃料電池に用いられる電極基材とその製造方法等に関するものである。

## 【0002】

【従来の技術】 燃料電池は、周知のように低排出物、高エネルギー効率で環境への負担の低い発電装置である。このため、近年の地球環境保護への高まりの中で再び脚光を浴びている。従来の大規模発電施設に比べ比較的小規模の分散型発電施設、自動車や船舶など移動体の発電装置、携帯電話など携帯電子機器の発電装置として、将来的にも期待されている発電装置である。燃料電池には、用いられる電解質の種類により、固体高分子型、リン酸型、固体酸化物型、熔融炭酸塩型、アルカリ型などの種類がある。なかでも固体高分子型燃料電池は、他の燃料電池に比べて、運転温度が低温で起動時間が短く、高出力が得やすい、小型軽量化が見込める、振動に強いなどの特徴を有し移動体の電力供給源に適している。さらに固体高分子型燃料電池の中でも、燃料に直接メタノール水溶液を供給する直接メタノール型燃料電池は、エネルギー密度が高く、携帯電子機器の電力供給源に適している。

【0003】 燃料電池は、発電を担う反応の起こるアノードとカソードの電極と、アノードとカソード間のイオン伝導体となる電解質とがそれぞれの間でセパレータで挟まれたセルをユニットとして構成されている。電極は、燃料拡散の促進と集（給）電を行う電極基材（集電体とも云う）と、実際に電気化学反応場となる電極触媒層とから構成されている。たとえば固体高分子型燃料電池のアノード電極では、燃料が触媒表面で反応してプロトンと電子を生じ、電子は電極基材に伝導し、プロトンは電解質のプロトン交換膜へと伝導する。このため、アノード電極には、燃料拡散性、電子伝導性、イオン伝導性が良好なことが要求される。一方、カソード電極では、酸化ガスが電極触媒層表面で、電解質から伝導してきたプロトンと、電極基材から伝導してきた電子とが反応して水を生成する。このため、ガス拡散性、電子伝導

性、イオン伝導性ととともに、生成した水を効率よく排出することも必要となる。

【0004】このような要求を満たすために、これまで電極基材にはさまざまな検討が加えられてきた。例えば、ガス拡散性を向上させた例として、特開平10-261421号公報や特開平11-273688号公報に記載の技術がこれまで報告されている。

【0005】これらの公報には、ガス拡散性向上を目的とした電極基材とするために、カーボンブラックの層を電極基材の表面に設けた例が、記載されている。また、電極基材（集電体）のその他の従来技術としては、特開平6-20710号公報、特開平7-326362号公報、あるいは、特開平7-220735号公報のものが提案されている。これらに開示された集電体は、短い長さの炭素繊維が炭素で結着されてなる多孔質炭素板からなるものである。

【0006】前述のように、電極は電極基材と電極触媒層とから構成されるが、これらの要求特性として、燃料拡散性、電子伝導性、イオン伝導性ととともに、生成した水を効率よく排出することが求められており、特に電極基材は、燃料拡散性、電子伝導性、排水性の点から多孔質導電シートが用いられている。このような多孔質導電シートの中でも、燃料拡散性向上と製造コスト低減のために、織物や、紙状の抄紙体、フェルトや不織布などの多孔質導電シートが用いられてきている。そして、このような多孔質導電シートからなる電極基材の表面に電極触媒層を塗布することが行われている。

【0007】この電極触媒層においては、前述の要求特性に加えて、用いられる触媒が例えば、白金、ルテニウムなどの高価な貴金属であるため、有効に用いられる触媒量の向上を図ることが必要である。特に上記のような多孔質導電シートからなる電極基材に電極触媒層を塗布する場合においては、電極基材への電極触媒層塗液の浸み込みが大きく、この浸み込みのために有効に用いられない無駄な触媒が多くなる原因となっていた。

【0008】ところで燃料電池は、移動体や携帯電子機器の電力供給源として期待されているが、自動車や携帯電話などの大量普及には大幅なコストダウンが必要である。特に電極触媒層中の触媒粒子においては、上記貴金属が用いられるために非常に高価であり、この触媒量を低減させることが強く求められている。このため、電極基材に浸み込んで有効に用いられない触媒をできるだけ減らすことが必要である。このような浸み込みを抑える手法として、特表平9-501541号公報には、触媒を含まない中間層を設けることが開示されている。ここでは、導電剤としてアセチレンブラックとプロトン導電ポリマとを含む中間層が触媒の浸み込み防止に効果を有することが開示されている。しかしながら、プロトン導電ポリマは、親水性ポリマであり水を含みやすいためカソードでの生成水の排出に支障を来すことが懸念され

る。

【0009】また、上述のカーボンブラック層を設けた電極基材は、表面のカーボンブラック層は平滑ではなく、よってその上に設けた電極触媒層が平滑にならない。このため、電極触媒層とプロトン交換膜との接合がよくなく、プロトン交換膜－電極触媒層間のプロトン伝導性が悪くなることが懸念される。

【0010】

【発明が解決しようとする課題】本発明は、上記課題、すなわち電極基材中への触媒の浸み込みを抑えることにより、無駄になる触媒量を低減させ、しかもカソードでの排水性能が良く、プロトン交換膜－電極触媒層間のプロトン伝導性についても高性能である電極基材およびその製造方法等を提供することを目的とする。

【0011】

【課題を解決するための手段】本発明は、上記課題を解決するために下記の構成を有する。

【0012】すなわち、本発明は、無機導電性繊維を含む多孔質の導電シートからなる電極基材において、該シートの電極触媒層を設ける側の表面粗さが、JIS B 0601で規定する中心線平均粗さ(Ra)で2μm以上20μm以下であることを特徴とする。

【0013】また、本発明の電極基材の製造方法は、上記シートの表面に、粘度が10Pa・s以上である無機導電性物質分散液を塗布することを特徴とする。

【0014】また、本発明の電気化学装置、水電解装置および燃料電池は、上記電極基材が適用されてなることを特徴とする。

【0015】さらに、本発明の移動体および携帯電子機器は、上記燃料電池を電力供給源としてなることを特徴とする。

【0016】

【発明の実施の形態】以下、本発明の好ましい実施の形態を図面を参照して説明する。

【0017】図1ないし図3は、本発明の電極基材5が用いられている種々の実施例の縦断面図であり、図1は本発明の電極基材5の表面に無機導電性物質層2が設けられた態様を、図2は図1の電極基材5の無機導電性物質層2の表面にさらに電極触媒層3が積層された態様を、図3はプロトン交換膜4を中心に図3の電極触媒層付き電極基材5が両側に設けられた態様の膜－電極複合体(MEA)を示している。なお、本発明の電極基材5は、図1のように通常は多孔質導電シート1の片面に無機導電性物質2を設けたものをいうが、図示は省略したが多孔質導電シート1の上に直接電極触媒層3を設けたものであっても良く、このようなものも本発明の電極基材に含まれる。

【0018】図1において、多孔質導電シート1は、燃料の拡散および電子の伝導を担うもので、特に限定されるものではないが、例えば導電性物質を主たる構成材と

することが好ましい。この導電性物質としては、ポリアクリロニトリルからの焼成体、ピッチからの焼成体、黒鉛及び膨張黒鉛などの炭素材、ステンレススチール、モリブデン、チタンなどが例示される。導電性物質の形態は繊維状あるいは粒子状など特に限定されないが、電極性能の点から繊維状の形態の無機導電性繊維が好ましい。なかでも燃料電池などの電気化学装置に用いる場合は、腐食と電気抵抗の点から、炭素繊維を用いるのが好ましい。

【0019】炭素繊維としては、その素材はポリアクリロニトリル(PAN)、ピッチ、あるいは低沸点有機化合物を原料とするものが好ましい。低沸点有機化合物とは例えば、ベンゼン、ナフタレン、クレオトル油などが例示できる。これらの中でも特にPAN系炭素繊維が好ましい。PAN系炭素繊維はピッチ系炭素繊維に比べて圧縮強さ、引張破断伸びが大きく、折れにくい。このことは炭素繊維を構成する炭素の結晶化の相異によると考えられる。折れにくい炭素繊維を得るためには、炭素繊維の熱処理温度は2,500℃以下が好ましく、2,000℃以下がより好ましい。

【0020】多孔質導電シート1の形態としては、織布あるいは不織布構造を有するシートいずれの構造でもよい。織布構造としては、無機導電性繊維のフィラメントを織ってなるフィラメント織布、紡績糸を織って織布とした後導電性を付与した紡績糸織布などを用いることができる。フィラメント織布の具体例としては、炭素繊維フィラメントを束ねてストランドにし、これを織ってなる炭素繊維フィラメント織布が挙げられ、紡績糸織布の具体例としては、PAN系繊維を紡績し、この紡績糸を織って織布とした後、焼成してなる炭素繊維紡績糸織布が挙げられる。また、不織布構造のシートとしては、抄紙体、フェルト、不織布など、繊維が不規則な構造を有しているシートが挙げられる。抄紙体は、繊維あるいは粒子とバインダーとを溶解または分散した液を用い、これを紙抄きの原理で網の上にすくい上げることにより得られる、薄く平らな紙状の構造体である。抄紙体が長さ10mm程度の短繊維を用いるのに対し、長さ25mm程度の比較的長い繊維を用いてこの繊維同士を絡めることにより得られるのがフェルトや不織布である。また、かぎ針状のもので繊維を引っかけて絡めたものがフェルト、空気流や水流で絡めたものが不織布となる。これらの布帛において、特に炭素繊維を用いた場合、耐炎化紡績糸を用いた平織物を炭化あるいは黒鉛化した織布、耐炎化糸をニードルパンチ法やウォータージェットパンチ法などによる不織布加工をした後に炭化あるいは黒鉛化した不織布、耐炎化糸あるいは炭化糸あるいは黒鉛化糸を用いた抄紙法によるマット不織布などが好ましく用いられる。例えば、東レ(株)製カーボンペーパーTGPシリーズ、SOシリーズ、E-TEK社製カーボンクロスなどである。また、導電性向上のために補助剤として

カーボンブラックなどの導電性粒子や、炭素繊維などの導電性繊維を添加することもできる。

【0021】これら多孔質導電シート1の目付としては、10~220g/m<sup>2</sup>が好ましく、より好ましくは20~120g/m<sup>2</sup>である。多孔質導電シート1の目付が10g/m<sup>2</sup>を下回ると多孔質導電シート1の強度が低くなる傾向がある。また、多孔質導電シート1表面に、無機導電性物質層2を設けることが困難になる。さらに、高分子電解質膜、触媒層、電極基材の一体化時や電池に組んだときに電極基材が薄くなり触媒層に埋没して面方向への拡散・透過効果が不十分になる傾向がある。一方、目付が220g/m<sup>2</sup>を越えると電池に組んだ時に電極基材が厚くなり抵抗が大きくなる。

【0022】所望により設ける無機導電性物質層2は、電極基材中への触媒の浸み込みを抑えることにより、無駄になる触媒量を低減させ、さらに上に設けた電極触媒層の表面を平滑にして、プロトン交換膜-電極触媒層間のプロトン伝導性を向上させるためのもので、その構成材としては、例えば、種々の黒鉛質や炭素質の単素材、あるいは、金属や半金属が挙げられる。本発明の電極を電気化学装置に用いる場合には、無機導電性物質としては、耐食性の観点から炭素材を用いることが好ましい。このような炭素材としては、オイルファーンズブラック、アセチレンブラック、サーマルブラック、チャネルブラックなどのカーボンブラックが、電子導電性と粒径から好ましい。オイルファーンズブラックとしては、キャボット社製バルカンXC-72、バルカンP、ブラックパールズ880、ブラックパールズ1100、ブラックパールズ1300、ブラックパールズ2000、リーガル400、ライオン社製ケッチェンブラックEC、三菱化学社製#3150、#3250などが挙げられ、アセチレンブラックとしては電気化学工業社製デンカブラックなどが挙げられる。上記の炭素材の中でも、無機導電性物質層の電気抵抗が低くなるという点で、キャボット社製バルカンXC-72、ライオン社製ケッチェンブラックEC、電気化学工業社製デンカブラック、あるいはこれらの混合物が好ましい。また、無機導電性物質層の構造は、特に限定されるものではないが、電子伝導性と燃料拡散性および排水性を良好にするためには、多孔質構造を有することは有効な実施態様である。特に、表面側が密であり、多孔質シート側が粗である非対称多孔質構造とすることは、触媒の浸み込みを抑えるためには、さらに好ましい実施態様である。無機導電性物質層を非対称多孔質構造とする方法は特に限定されないが、例えば、多孔質シート側に嵩高い無機導電性物質を設け、表面側により嵩の低い無機導電性物質を設けることにより、非対称多孔質構造を発現させることができる。また、無機導電性物質を、無機導電性物質層の構造を実質的に維持する樹脂溶液に分散させ、この分散液を多孔質シートに塗布した後、樹脂溶液に混和する樹脂を溶

解させにくいいわゆる樹脂に対する貧溶媒に浸漬する、いわゆる湿式凝固法においても、非対称多孔質構造を発生させることができる。無機導電性物質の嵩高さは、無機導電性物質の比表面積 ( $\text{m}^2/\text{g}$ ) をもって評価することができる。すなわち、比表面積が低い無機導電性物質の方が、より嵩高い無機導電性物質である。無機導電性物質の比表面積の測定方法は特に限定されないが、例えば窒素吸着法により求めることができる。窒素吸着法とは、脱気した無機導電性物質を液体窒素に浸漬させ、平衡時における無機導電性物質表面に吸着した窒素量を測定し、この値から比表面積を算出する手法のことである。無機導電性物質の比表面積は好ましくは  $1\text{m}^2/\text{g} \sim 2000\text{m}^2/\text{g}$ 、より好ましくは  $10\text{m}^2/\text{g} \sim 1000\text{m}^2/\text{g}$  である。比表面積は、前記数値範囲の上限値を上回ると無機導電性物質の製造が困難になり、前記数値範囲の下限を下回ると無機導電性物質層の表面粗さを前記数値範囲の上限値以下にすることが困難となり、好ましくないことがある。

【0023】また、無機導電性物質層2が、表面側が密であり、多孔質シート側が粗である非対称多孔質構造である場合には、密な側の無機導電性物質の比表面積を  $S_A (\text{m}^2/\text{g})$ 、粗な側の無機導電性物質の比表面積を  $S_B (\text{m}^2/\text{g})$  とすると、これらの関係が  $1 < S_A/S_B \leq 2000$ 、より好ましくは  $1.1 \leq S_A/S_B \leq 100$  であることが好ましい。ここで  $S_A/S_B$  が前記数値範囲の上限値を上回ると、密な側の無機導電性物質層の燃料拡散性が悪くなって好ましくなく、また、 $S_A/S_B$  が前記数値範囲の下限値を下回るとは、実質的に無機導電性物質層が非対称多孔質構造とならないことを意味する。

$$R_a = \frac{1}{l} \int_0^l |f(x)| dx$$

【0027】上記中心線平均粗さ  $R_a$  を測定する装置は、JIS B0601に準じた測定のできる表面粗さ測定器であれば特に限定はされないが、例えば、(株)キーエンス製超深度表面形状測定顕微鏡 (形式: VK-8500) や、

(株)小坂研究所製表面粗さ測定器 (形式: SE-3300) を用いることができる。

【0028】また、無機導電性物質の形態は粒子状であることが望ましい。粒子状以外の形態であると、無機導電性物質層2の前述した表面粗さを前記数値範囲の上限値以下に設定しにくくなる傾向があるためである。この粒径としては、好ましくは  $10\text{nm} \sim 20\mu\text{m}$ 、より好ましくは  $20\text{nm} \sim 100\text{nm}$  である。粒径が前記数値範囲の下限値を下回ると無機導電性物質の製造が困難になり、一方、前記数値範囲の上限値を上回ると無機導電

【0024】ところで、本発明は、上述したように電極基材5として、電子伝導性、燃料拡散性そして排水性に優れた多孔質導電シート1を用いる際に、問題となる該基材中への触媒の浸み込みを極力抑制することを目的とし、そのために電極基材の電極触媒層3側表面、すなわち電極基材5として、図1または図2で説明した電極基材1の片面に無機導電性物質層2を設ける態様のものを採用する場合には無機導電性物質層2の電極触媒層3側表面を、また、多孔質導電シート1の表面に直接電極触媒層3を設ける態様のものを採用する場合には電極触媒層1の電極触媒層3側表面の表面粗さを、 $2\mu\text{m}$ 以上 $20\mu\text{m}$ 以下にすることを特徴とするものである。もし、電極基材の表面粗さが $2\mu\text{m}$ を下回ると、電極基材の燃料拡散性が悪くなる傾向があり、 $20\mu\text{m}$ を越えると、電極基材への触媒の浸み込みが多くなって好ましくない。このようなことから、より好ましい表面粗さは $3\mu\text{m}$ 以上 $15\mu\text{m}$ 以下である。かかる表面粗さにすると、さらに燃料拡散性と電極基材への触媒浸み込み阻止性が向上する。

【0025】ここで、本発明で言う表面粗さとは、JIS B0601で規定する表面粗さの規格のうち、中心線平均粗さ ( $R_a$ ) として定義するものである。この中心線平均粗さ ( $R_a$ ) は、粗さ曲線からその中心線の方に測定長さ  $l$  の部分を抜き取り、この抜き取り部分の中心線を  $X$  軸、縦倍率の方向を  $Y$  軸、粗さ曲線を  $y=f(x)$  で表したとき、次の式によって求められる値をマイクロメートル ( $\mu\text{m}$ ) で表したものである。

【0026】

【数1】

性物質層の表面粗さを前記数値範囲の上限値以下にすることが困難となる傾向がある。

【0029】次に、本発明の電極基材の製造方法の一実施態様例について、説明する。

【0030】まず、耐炎化紡績糸を用いて平織物を作成し、この平織物を炭化することにより炭素繊維織物を作成する。これは図1、2における多孔質導電シート1に相当する。次に、無機導電性物質の分散液を炭素繊維織物上に塗布して、無機導電性物質層を形成する。これは図1、2における無機導電性物質層2に相当する。この無機導電性物質層をプレスまたは研磨することにより、表面粗さをJIS B0601における中心線平均粗さ ( $R_a$ ) で $2\mu\text{m}$ 以上 $20\mu\text{m}$ 以下にする。次に、電極触媒分散液を無機導電性物質層上に塗布して、電極触媒



層を作成する。これは図2における電極触媒層3に相当する。

【0031】多孔質導電シートに無機導電性物質を積層する方法としては、シート表面に分散液を塗布して製造することも好ましく、さらに無機導電性物質分散液の粘度としては $10\text{Pa}\cdot\text{s}$ 以上、より好ましくは $20\text{Pa}\cdot\text{s}$ 以上であるのが好ましい。無機導電性物質分散液の粘度が $10\text{Pa}\cdot\text{s}$ を下回ると、多孔質導電シートに塗布した際に無機導電性物質がシート内に浸み込み易くなり、多孔質導電シート表面に無機導電性物質層を設けることが困難になる傾向がある。無機導電性物質分散液には、界面活性剤を添加することもできる。界面活性剤を添加することにより、無機導電性物質が分散液になじみやすくなり、分散液が安定化する効果が得られる。また、無機導電性物質分散液の粘度を下げる効果があり、すなわち同じ粘度の無機導電性物質分散液でも界面活性剤を添加することにより、より無機導電性物質の濃度を高くすることができる。

【0032】無機導電性物質分散液の粘度は、JIS K5400で規定する「塗料一般試験方法4.5.3 回転粘度計法」に準じて測定することができる。粘度を測定する装置は特に限定されるものではないが、例えば、(株)東京計器製B型粘度計B8Lを用いることができる。

【0033】本発明における電極基材の製造方法としては特に限定されるものではないが、多孔質導電シート1表面に無機導電性物質層2を設けた後、表面をプレスして製造することも好ましい実施態様である。プレスの方法としては特に限定されるものではないが、ロールプレス、平板プレスなどを用いることができる。また、プレス効率を高めるために、加熱することも好ましい実施態様である。プレスの圧力としては $0.1\text{MPa}$ 以上 $10\text{MPa}$ 以下、より好ましくは $1\text{MPa}$ 以上 $5\text{MPa}$ 以下であることが好ましい。圧力が前記数値範囲の下限値を下回ると、無機導電性物質層の表面に設ける電極触媒層塗液の浸み込みが多くなって好ましくなく、前記数値範囲の上限値を上回ると、無機導電性物質層の燃料拡散性が悪くなって好ましくない。プレスの温度としては、無機導電性物質層が変形しやすい温度であれば、特に限定されるものではない。また、無機導電性物質層が変形しやすい温度は、無機導電性物質層を構成する物質に依存し、一概には特定し難いが、例えば無機導電性物質層にPTFEが含まれる場合には、 $327^{\circ}\text{C}$ 以上 $400^{\circ}\text{C}$ 以下、より好ましくは $350^{\circ}\text{C}$ 以上 $390^{\circ}\text{C}$ 以下が好ましく、四フッ化エチレン-パーフルオロビニルエーテル共重合体(PFA)が含まれる場合には、 $310^{\circ}\text{C}$ 以上 $400^{\circ}\text{C}$ 以下、より好ましくは $330^{\circ}\text{C}$ 以上 $390^{\circ}\text{C}$ 以下が好ましく、四フッ化エチレン-六フッ化プロピレン共重合体(FEP)が含まれる場合には、 $250^{\circ}\text{C}$ 以上 $320^{\circ}\text{C}$ 以下、より好ましくは $270^{\circ}\text{C}$ 以上 $300^{\circ}\text{C}$ 以下が好ましい。プレス温度が前記数値範囲の下限値を下回

ると、無機導電性物質層が変形しにくくなって好ましくなく、前記数値範囲の上限値を上回ると、無機導電性物質層の中のフッ素化合物が分解しやすくなる傾向がある。無機導電性物質層2に界面活性剤が含まれる場合は、プレス前に界面活性剤の分解温度にまで加熱して予備焼成を行い、界面活性剤を分解させることも、無機導電性物質層の燃料透過性を向上させる上で好ましい実施態様である。

【0034】さらに、多孔質導電シート表面に無機導電性物質層を設けた後、表面を研磨して製造することも好ましい実施態様である。研磨基材としては特に限定されるものではないが、研磨布、研磨紙、研磨ベルト、研磨シート、研磨ディスク、ブラシロールなどを用いることができる。また、研磨材としては特に限定されるものではないが、アルミナ、ジルコニア、溶融アルミナ、炭化けい素、ガーネット、エメリーなどを用いることができる。

【0035】図1、2の本発明の多孔質導電シートからなる電極基材、あるいは該電極基材と電極触媒層、図3の固体電解質膜から構成される膜-電極複合体(MEA)は、種々の電気化学装置に適用することができる。なかでも、水電解装置や燃料電池が好ましく、さらに燃料電池の中でも、固体高分子型燃料電池や直接メタノール型燃料電池に好適である。

【0036】さらに、本発明の電極基材を用いた燃料電池の用途としては、特に限定されることなく考えられるが、固体高分子型燃料電池において有用な用途である移動体の電力供給源が好ましいものである。特に、乗用車、バス、トラックなどの自動車や、船舶、鉄道なども好ましい移動体である。さらに直接メタノール型燃料電池において有用な用途である携帯電子機器の電力供給源も好ましいものである。特に、携帯電話やコンピューター、ナビゲーションシステムなども好ましい携帯電子機器である。

#### 【0037】

【実施例】以下、図1ないし図3、実施例および比較例により、本発明を詳細に説明するが、本発明はこれらに限定されるものでない。また、以下の実施例および比較例において、粘度は全て(株)東京計器製B型粘度計B8Lを用い、 $25^{\circ}\text{C}$ の温度において測定を行い、表面粗さは全て(株)キーエンス製超深度表面形状測定顕微鏡VK-8500を用いて測定を行った。

#### 【0038】実施例1

##### (1) 無機導電性物質分散液の作成

図1の無機導電性物質層2として、無機導電性物質を得るため、界面活性剤(TRITON X-114、ナカライテスク(株)より購入)  $12\text{g}$ 、アセチレンブラック(DENKA BLACK、電気化学工業(株)製、窒素比表面積 $61\text{m}^2/\text{g}$ )  $6\text{g}$ 、PTFE水分散液(ポリフロンPTFE、ダイキン工業(株)製)  $2.5$

g、水39.5gを混合し、ホモジナイザーで十分にかくはんした。得られた分散液の粘度は、 $800\text{Pa}\cdot\text{s}$ であった。

#### 【0039】(2) 電極基材の作成

また、多孔質導電シート1として、炭素繊維織物（E-TEK製クロス、タイプA、目付け $116\text{g}/\text{m}^2$ ）にPTFE水分散液（ポリフロンPTFE、ダイキン工業（株）製）を含浸、乾燥させた。得られた織物のPTFE含有率は $20\text{wt}\%$ であった。この織物の片面に

(1) で作成した分散液を塗布し、直ちに $100^\circ\text{C}$ にて乾燥させた。得られた織物のアセチレンブラック付き量は $2\text{mg}/\text{cm}^2$ であった。この織物に $380^\circ\text{C}$ 、 $3\text{MPa}$ の圧力をかけ、 $3\text{MPa}$ の圧力を保ったまま15分間かけて室温に冷却するプレスを行い、電極基材を得た。得られた電極基材の無機導電性物質が付着している側（平滑な側）の表面粗さは $9\mu\text{m}$ であった。

#### 【0040】(3) 電極触媒層付き電極基材の作成

Aldrich社製Nafion溶液に、触媒担持カーボン（触媒：Pt、カーボン：Cabot社製ValcanXC-72、白金担持量：50重量%）を、白金とNafionの重量比が $1:0.5$ になるように加え、よく攪拌して触媒-ポリマ組成物を調製した。この触媒-ポリマ組成物を、(2) で作成した電極基材の平滑な側に塗布し、直ちに乾燥して、電極触媒層付き電極基材5を作成した。得られた電極触媒層付き電極基材の電極触媒層は、白金の付着量 $0.5\text{mg}/\text{cm}^2$ であった。

#### 【0041】(4) 膜-電極接合体の作成および評価

図3の膜-電極接合体として、上記(3)で作成した2枚の電極触媒層付き電極基材の間に、プロトン交換膜（DuPont社製Nafion112）を、電極触媒層がプロトン交換膜に接するように挟み、 $130^\circ\text{C}$ 、 $5\text{MPa}$ の条件でホットプレスし、接合体とした。得られた接合体を燃料電池セルに組み込み、常圧（大気圧）の水素および空気を供給し、運転温度 $70^\circ\text{C}$ の条件で、電流-電圧（I-V）特性を測定した。最高出力は $450\text{mW}/\text{cm}^2$ であり、優れた高出力特性を示した。

#### 【0042】比較例1

##### (1) 電極基材の作成

炭素繊維織物（E-TEK製クロス、タイプA、目付け $116\text{g}/\text{m}^2$ ）にPTFE水分散液（ポリフロンPTFE、ダイキン工業（株）製）を含浸、乾燥後、 $380^\circ\text{C}$ にて焼成を行った。得られた電極基材のPTFE含有率は $20\text{wt}\%$ であり、表面粗さは $30\mu\text{m}$ であった。

#### 【0043】(2) 電極触媒層付き電極基材の作成

上記(1)で作成した電極基材の片面に、実施例1(3)と同様にして触媒-ポリマ組成物を塗布し、直ちに乾燥して、電極触媒層付き電極基材を作成した。得られた電極触媒層付き電極基材の電極触媒層は、白金の付着量 $0.5\text{mg}/\text{cm}^2$ であった。

#### 【0044】(3) 膜-電極接合体の作成および評価

上記(2)で作成した電極触媒層付き電極基材を用いて、実施例1(4)と同様にして膜-電極接合体を作成し、I-V特性を測定した。最高出力は $100\text{mW}/\text{cm}^2$ であり、実施例1よりも劣る出力特性であった。電極基材の表面粗さが実施例1に比べて粗く、電極触媒層が電極基材にしみ込み、プロトン交換膜と電極触媒との間に良好な接合界面を形成できなかったためと考えられる。

#### 【0045】比較例2

##### (1) 電極基材の作成

炭素繊維織物（E-TEK製クロス、タイプA、目付け $116\text{g}/\text{m}^2$ ）にPTFE水分散液（ポリフロンPTFE、ダイキン工業（株）製）を含浸、乾燥させた。得られた織物のPTFE含有率は $20\text{wt}\%$ であった。この織物の片面に実施例1(1)で作成した分散液を塗布し、直ちに $100^\circ\text{C}$ にて乾燥させた。この織物を $380^\circ\text{C}$ で焼成した。得られた織物のアセチレンブラック付き量は $2\text{mg}/\text{cm}^2$ であり、無機導電性物質が付着している側の表面粗さは $25\mu\text{m}$ であった。

#### 【0046】(2) 電極触媒層付き電極基材の作成

上記(1)で作成した電極基材の無機導電性物質が付着している側に、実施例1(3)と同様にして触媒-ポリマ組成物を塗布し、直ちに乾燥して、電極触媒層付き電極基材を作成した。得られた電極触媒層付き電極基材の電極触媒層は、白金の付着量 $0.5\text{mg}/\text{cm}^2$ であった。

#### 【0047】(3) 膜-電極接合体の作成および評価

上記(2)で作成した電極触媒層付き電極基材を用いて、実施例1(4)と同様にして膜-電極接合体を作成し、I-V特性を測定した。最高出力は $200\text{mW}/\text{cm}^2$ であり、実施例1よりも劣る出力特性であった。電極基材の表面粗さが実施例1に比べて粗く、電極触媒層が電極基材にしみ込み、プロトン交換膜と電極触媒との間に良好な接合界面を形成できなかったためと考えられる。

#### 【0048】比較例3

##### (1) 電極基材の作成

炭素繊維織物（E-TEK製クロス、タイプA、目付け $116\text{g}/\text{m}^2$ ）にPTFE水分散液（ポリフロンPTFE、ダイキン工業（株）製）を含浸、乾燥させた。得られた織物のPTFE含有率は $20\text{wt}\%$ であった。この織物の片面に実施例1(1)で作成した分散液を塗布し、直ちに $100^\circ\text{C}$ にて乾燥させた。得られた織物のアセチレンブラック付き量は $5\text{mg}/\text{cm}^2$ であった。この織物に $380^\circ\text{C}$ 、 $100\text{MPa}$ の圧力をかけ、 $100\text{MPa}$ の圧力を保ったまま15分間かけて室温に冷却するプレスを行い、電極基材を得た。得られた電極基材の無機導電性物質が付着している側（平滑な側）の表面粗さは $1\mu\text{m}$ であった。

#### 【0049】(2) 電極触媒層付き電極基材の作成

上記(1)で作成した電極基材の片面に、実施例1

(3)と同様にして触媒-ポリマ組成物を塗布し、直ちに乾燥して、電極触媒層付き電極基材を作成した。得られた電極触媒層付き電極基材の電極触媒層は、白金の付着量 $0.5\text{mg}/\text{cm}^2$ であった。

【0050】(3)膜-電極接合体の作成および評価  
上記(2)で作成した電極触媒層付き電極基材を用いて、実施例1(4)と同様にして膜-電極接合体を作成し、I-V特性を測定した。最高出力は $100\text{mW}/\text{cm}^2$ であり、実施例1よりも劣る出力特性であった。電極基材の表面粗さが実施例1に比べて細かく、生成水が電極基材に詰まってガス拡散性が悪くなったためと考えられる。

#### 【0051】比較例4

##### (1)無機導電性物質分散液の作成

界面活性剤(TRITON X-114、ナカライテスク(株)より購入)  $0.5\text{g}$ 、アセチレンブラック(DENKA BLACK、電気化学工業(株)製、粒径 $42\text{nm}$ )  $2\text{g}$ 、PTFE水分散液(ポリフロンPTFE、ダイキン工業(株)製)  $0.83\text{g}$ 、水 $12.9\text{g}$ を混合し、ホモジナイザーで十分にかくはんした。得られた分散液の粘度は、 $1\text{Pa}\cdot\text{s}$ であった。

##### 【0052】(2)電極基材の作成

炭素繊維織物(E-TEK製クロス、タイプA、目付け $116\text{g}/\text{m}^2$ )にPTFE水分散液(ポリフロンPTFE、ダイキン工業(株)製)を含浸、乾燥させた。得られた織物のPTFE含有率は $20\text{wt}\%$ であった。この織物の片面に(1)で作成した分散液を塗布し、直ちに $100^\circ\text{C}$ にて乾燥させた。得られた織物のアセチレンブラック付き量は $2\text{mg}/\text{cm}^2$ であった。この織物に $380^\circ\text{C}$ 、 $3\text{MPa}$ の圧力をかけ、 $3\text{MPa}$ の圧力を保ったまま15分間かけて室温に冷却するプレスを行い、電極基材を得た。得られた電極基材の無機導電性物質が付着している側の表面粗さは $25\mu\text{m}$ であった。

##### 【0053】(3)電極触媒層付き電極基材の作成

上記(2)で作成した電極基材の無機導電性物質が付着している側に、実施例1(3)と同様にして触媒-ポリマ組成物を塗布し、直ちに乾燥して、電極触媒層付き電極基材を作成した。得られた電極触媒層付き電極基材の電極触媒層は、白金の付着量 $0.5\text{mg}/\text{cm}^2$ であった。

##### 【0054】(4)膜-電極接合体の作成および評価

上記(3)で作成した電極触媒層付き電極基材を用いて、実施例1(4)と同様にして膜-電極接合体を作成し、I-V特性を測定した。最高出力は $200\text{mW}/\text{cm}^2$ であり、実施例1よりも劣る出力特性であった。無機導電性物質分散液の粘度が実施例1に比べて低く、無機導電性物質が織物にしみ込んだため、電極基材の表面粗さが実施例1に比べて粗くなり、電極触媒層が電極基材にしみ込み、プロトン交換膜と電極触媒との間に良好

な接合界面を形成できなかったためと考えられる。

#### 【0055】実施例2

##### (1)電極基材の作成

炭素繊維織物(E-TEK製クロス、タイプA、目付け $116\text{g}/\text{m}^2$ )にPTFE水分散液(ポリフロンPTFE、ダイキン工業(株)製)を含浸、乾燥させた。得られた織物のPTFE含有率は $20\text{wt}\%$ であった。この織物の片面に実施例1(1)で作成した分散液を塗布し、直ちに $100^\circ\text{C}$ にて乾燥させた。得られた織物のアセチレンブラック付き量は $2\text{mg}/\text{cm}^2$ であった。この織物を $280^\circ\text{C}$ のオーブンで2時間かけて脱界面活性剤処理を行った。この織物に $380^\circ\text{C}$ 、 $3\text{MPa}$ の圧力をかけ、 $3\text{MPa}$ の圧力を保ったまま15分間かけて室温に冷却するプレスを行い、電極基材を得た。得られた電極基材の無機導電性物質が付着している側(平滑な側)の表面粗さは $9\mu\text{m}$ であった。

##### 【0056】(2)電極触媒層付き電極基材の作成

上記(1)で作成した電極基材の無機導電性物質が付着している側に、実施例1(3)と同様にして触媒-ポリマ組成物を塗布し、直ちに乾燥して、電極触媒層付き電極基材を作成した。得られた電極触媒層付き電極基材の電極触媒層は、白金の付着量 $0.5\text{mg}/\text{cm}^2$ であった。

##### 【0057】(3)膜-電極接合体の作成および評価

上記(2)で作成した電極触媒層付き電極基材を用いて、実施例1(4)と同様にして膜-電極接合体を作成し、I-V特性を測定した。最高出力は $450\text{mW}/\text{cm}^2$ であり、優れた高出力特性を示した。

#### 【0058】実施例3

##### (1)電極基材の作成

カーボンペーパー(東レ(株)製、TGP-H-060、目付け $83\text{g}/\text{m}^2$ )にPTFE水分散液(ポリフロンPTFE、ダイキン工業(株)製)を含浸、乾燥させた。得られたカーボンペーパーのPTFE含有率は $20\text{wt}\%$ であった。このカーボンペーパーの片面に実施例1(1)で作成した分散液を塗布し、直ちに $100^\circ\text{C}$ にて乾燥させた。得られたカーボンペーパーのアセチレンブラック付き量は、 $1\text{mg}/\text{cm}^2$ であった。このカーボンペーパーに $380^\circ\text{C}$ 、 $3\text{MPa}$ の圧力をかけ、 $3\text{MPa}$ の圧力を保ったまま15分間かけて室温に冷却するプレスを行い、電極基材を得た。得られた電極基材の無機導電性物質が付着している側(平滑な側)の表面粗さは $9\mu\text{m}$ であった。

##### 【0059】(2)電極触媒層付き電極基材の作成

上記(1)で作成した電極基材の無機導電性物質が付着している側に、実施例1(3)と同様にして触媒-ポリマ組成物を塗布し、直ちに乾燥して、電極触媒層付き電極基材を作成した。得られた電極触媒層付き電極基材の電極触媒層は、白金の付着量 $0.5\text{mg}/\text{cm}^2$ であった。

【0060】(3) 膜-電極接合体の作成および評価  
上記(2)で作成した電極触媒層付き電極基材を用いて、実施例1(4)と同様にして膜-電極接合体を作成し、I-V特性を測定した。最高出力は450mW/cm<sup>2</sup>であり、優れた高出力特性を示した。

#### 【0061】比較例5

##### (1) 電極基材の作成

カーボンペーパー(東レ(株)製、TGP-H-060、目付け83g/m<sup>2</sup>)にPTFE水分散液(ポリフロンプTFE、ダイキン工業(株)製)を含浸、乾燥後、380℃にて焼成を行った。得られた電極基材のPTFE含有率は20wt%であり、表面粗さは21μmであった。

【0062】(2) 電極触媒層付き電極基材の作成  
上記(1)で作成した電極基材の片面に、実施例1(3)と同様にして触媒-ポリマ組成物を塗布し、直ちに100℃にて乾燥して、電極触媒層付き電極基材を作成した。得られた電極触媒層付き電極基材の電極触媒層は、白金の付着量0.5mg/cm<sup>2</sup>であった。

【0063】(3) 膜-電極接合体の作成および評価  
上記(2)で作成した電極触媒層付き電極基材を用いて、実施例1(4)と同様にして膜-電極接合体を作成し、I-V特性を測定した。最高出力は350mW/cm<sup>2</sup>であり、実施例3よりも劣る出力特性であった。電極基材の表面粗さが実施例3に比べて粗く、電極触媒層が電極基材にしみ込み、プロトン交換膜と電極触媒との間に良好な接合界面を形成できなかったためと考えられる。

#### 【0064】比較例6

##### (1) 電極基材の作成

長さ12mmにカットしたPAN系炭素繊維(直径7μm)の短繊維を水中で分散、金網上に抄造し、炭素短繊維を結着する高分子物質であるポリビニルアルコールと酢酸ビニルの混合物からなるエマルジョンを付着させて乾燥し、炭素繊維紙からなる多孔質導電シートを得た。この炭素繊維紙を焼成し、目付5g/m<sup>2</sup>のカーボンペーパーを得た。このカーボンペーパーに、PTFE水分散液(ポリフロンプTFE、ダイキン工業(株)製)を含浸、乾燥させた。得られた多孔質導電シートのPTFE含有率は20wt%であった。この多孔質導電シートの片面に実施例1(1)で作成した分散液を塗布しようとしたが、うまく塗布することができず、無機導電性物質層を形成することができなかった。多孔質導電シートの目付けが低すぎたためと考えられる。

#### 【0065】実施例4

(1) 比表面積の小さい無機導電性物質分散液の作成  
界面活性剤(TRITON X-114、ナカライテスク(株)より購入)12g、アセチレンブラック(DENKA BLACK、電気化学工業(株)製、窒素比表面積61m<sup>2</sup>/g)6g、PTFE水分散液(ポリフロ

ンプTFE、ダイキン工業(株)製)2.5g、水39.5gを混合し、ホモジナイザーで十分にかくはんした。得られた分散液の粘度は、800Pa・sであった。

【0066】(2) 比表面積の大きい無機導電性物質分散液の作成

界面活性剤(TRITON X-114、ナカライテスク(株)より購入)12g、オイルファーンブラック(ValcanXC-72、Cabot社製、窒素比表面積254m<sup>2</sup>/g)6g、PTFE水分散液(ポリフロンプTFE、ダイキン工業(株)製)2.5gを混合し、ホモジナイザーで十分にかくはんした。得られた分散液の粘度が100Pa・sとなるように、水を加えて調整した。

【0067】(3) 無機導電性物質の表面側が密である非対称構造に形成された電極基材の作成

##### 比較例1

上記(1)で作成した電極基材の片面に(1)で作成した比表面積の小さい無機導電性物質分散液を塗布し、直ちに100℃にて乾燥させた。得られた織物のアセチレンブラック付き量は1mg/cm<sup>2</sup>であった。その上に、さらに(2)で作成した比表面積の大きい無機導電性物質分散液を塗布し、直ちに100℃にて乾燥させた。得られた織物のオイルファーンブラック付き量は1mg/cm<sup>2</sup>であった。このようにして、無機導電性物質の表面側が密である非対称構造に形成された電極基材を得た。得られた電極基材の無機導電性物質が付着している側(平滑な側)の表面粗さは10μmであった。

【0068】(4) 電極触媒層付き電極基材の作成

上記(3)で作成した電極基材の無機導電性物質が付着している側に、実施例1(3)と同様にして触媒-ポリマ組成物を塗布し、直ちに乾燥して、電極触媒層付き電極基材を作成した。得られた電極触媒層付き電極基材の電極触媒層は、白金の付着量0.5mg/cm<sup>2</sup>であった。

【0069】(5) 膜-電極接合体の作成および評価  
上記(4)で作成した電極触媒層付き電極基材を用いて、実施例1(4)と同様にして膜-電極接合体を作成し、I-V特性を測定した。最高出力は450mW/cm<sup>2</sup>であり、優れた高出力特性を示した。

#### 【0070】実施例5

(1) 比表面積の小さい無機導電性物質分散液の作成  
界面活性剤(TRITON X-114、ナカライテスク(株)より購入)12g、アセチレンブラック(DENKA BLACK、電気化学工業(株)製、窒素比表面積61m<sup>2</sup>/g)6g、PTFE水分散液(ポリフロンプTFE、ダイキン工業(株)製)2.5g、水39.5gを混合し、ホモジナイザーで十分にかくはんした。得られた分散液の粘度は、800Pa・sであった。

【0071】(2) 比表面積の大きい無機導電性物質分

#### 散液の作成

界面活性剤 (TRITON X-114、ナカライテスク (株) より購入) 12 g、オイルファーネスブラック (ケッチェンブラック EC、ライオン社製、窒素比表面積 1000 m<sup>2</sup>/g) 6 g、PTFE 水分散液 (ポリフロンプTFE、ダイキン工業 (株) 製) 2.5 g を混合し、ホモジナイザーで十分にかくはんした。得られた分散液の粘度が 100 Pa・s となるように、水を加えて調整した。

【0072】(3) 無機導電性物質の表面側が密である非対称構造に形成された電極基材の作成

#### 比較例 1

上記 (1) で作成した電極基材の片面に (1) で作成した比表面積の小さい無機導電性物質分散液を塗布し、直ちに 100℃ にて乾燥させた。得られた織物のアセチレンブラック付き量は 1 mg/cm<sup>2</sup> であった。その上に、さらに (2) で作成した比表面積の大きい無機導電性物質分散液を塗布し、直ちに 100℃ にて乾燥させた。得られた織物のオイルファーネスブラック付き量は 1 mg/cm<sup>2</sup> であった。このようにして、無機導電性物質の表面側が密である非対称構造に形成された電極基材を得た。得られた電極基材の無機導電性物質が付着している側 (平滑な側) の表面粗さは 10 μm であった。

【0073】(4) 電極触媒層付き電極基材の作成

(3) で作成した電極基材の無機導電性物質が付着している側に、実施例 1 (3) と同様にして触媒-ポリマ組成物を塗布し、直ちに乾燥して、電極触媒層付き電極基材を作成した。得られた電極触媒層付き電極基材の電極触媒層は、白金の付着量 0.5 mg/cm<sup>2</sup> であった。

(5) 膜-電極接合体の作成および評価

(4) で作成した電極触媒層付き電極基材を用いて、実施例 1 (4) と同様にして膜-電極接合体を作成し、I-V 特性を測定した。最高出力は 450 mW/cm<sup>2</sup> であり、優れた高出力特性を示した。

【0074】実施例 6

(1) 電極基材の作成

比較例 2 (1) で作成した電極基材の無機導電性物質が付着している側の表面を、紙ヤスリ (1000 番手) で研磨した。得られた電極基材の無機導電性物質が付着している側の表面粗さは 10 μm であった。

【0075】(2) 電極触媒層付き電極基材の作成

上記 (1) で作成した電極基材の無機導電性物質が付着している側に、実施例 1 (3) と同様にして触媒-ポリマ組成物を塗布し、直ちに乾燥して、電極触媒層付き電極基材を作成した。得られた電極触媒層付き電極基材の電極触媒層は、白金の付着量 0.5 mg/cm<sup>2</sup> であった。

【0076】(3) 膜-電極接合体の作成および評価

上記 (2) で作成した電極触媒層付き電極基材を用いて、実施例 1 (4) と同様にして膜-電極接合体を作成

し、I-V 特性を測定した。最高出力は 450 mW/cm<sup>2</sup> であり、優れた高出力特性を示した。

【0077】実施例 7

(1) 多孔質構造を有する電極触媒層付き電極基材の作成

Aldrich 社製 Nafion 溶液に、触媒担持カーボン (触媒: Pt、カーボン: Cabot 社製 Vulcan XC-72、白金担持量: 50 重量%) を、白金と Nafion の重量比が 1:0.5 になるように加え、よく攪拌して触媒-ポリマ組成物を調製した。この触媒-ポリマ組成物を、実施例 1 (1) および (2) で作成した電極基材の平滑な側に塗布し、直ちに酢酸ブチルに浸漬して、三次元網目多孔質構造を有する電極触媒層が付いた電極基材を作成した。得られた電極触媒層付き電極基材の電極触媒層は、白金の付着量 0.5 mg/cm<sup>2</sup> であった。

【0078】(2) 膜-電極接合体の作成および評価

上記 (1) で作成した電極触媒層付き電極基材を用いて、実施例 1 (4) と同様にして膜-電極接合体を作成し、I-V 特性を測定した。最高出力は 500 mW/cm<sup>2</sup> であり、優れた高出力特性を示した。

【0079】実施例 8

(1) 電極触媒層付き電極基材の作成

Aldrich 社製 Nafion 溶液に、触媒担持カーボン (触媒: Pt·Ru、カーボン: ライオン社製 ケッチェンブラック EC、白金担持量: 30 重量%、ルテニウム担持量: 24 重量%) を、カーボンと Nafion の重量比が 1:0.5 になるように加え、よく攪拌して触媒-ポリマ組成物を調製した。この触媒-ポリマ組成物を、実施例 1 (2) で作成した電極基材の平滑な側に塗布し、直ちに乾燥して、電極触媒層付き電極基材を作成した。得られた電極触媒層付き電極基材の電極触媒層は、白金の付着量 1.0 mg/cm<sup>2</sup> であった。

【0080】(2) 膜-電極接合体の作成および評価

上記 (1) で作成した電極触媒層付き電極基材および実施例 1 (3) で作成した電極触媒層付き電極基材の間に、プロトン交換膜 (DuPont 社製 Nafion 112) を、電極触媒層がプロトン交換膜に接するように挟み、130℃、5 MPa の条件でホットプレスし、接合体とした。得られた接合体を燃料電池セルに組み込み、常圧 (大気圧) の 50 mol% メタノール水溶液および空気を供給し、運転温度 25℃ の条件で、電流-電圧 (I-V) 特性を測定した。最高出力は 50 mW/cm<sup>2</sup> であり、優れた高出力特性を示した。

【0081】比較例 7

(1) 電極触媒層付き電極基材の作成

Aldrich 社製 Nafion 溶液に、触媒担持カーボン (触媒: Pt·Ru、カーボン: ライオン社製 ケッチェンブラック EC、白金担持量: 30 重量%、ルテニウム担持量: 24 重量%) を、カーボンと Nafion の重量比が 1:0.5 になるように加え、よく攪拌して触媒-ポリマ組成物を調

製した。この触媒-ポリマ組成物を、比較例 2 (1) で作成した電極基材の無機導電性物質が付着している側に塗布し、直ちに乾燥して、電極触媒層付き電極基材を作成した。得られた電極触媒層付き電極基材の電極触媒層は、白金の付着量  $1.0 \text{ mg/cm}^2$  であった。

【0082】(2) 膜-電極接合体の作成および評価  
上記 (1) で作成した電極触媒層付き電極基材および比較例 2 (2) で作成した電極触媒層付き電極基材を用いて、実施例 7 (2) と同様にして膜-電極接合体を作成し、I-V 特性を測定した。最高出力は  $20 \text{ mW/cm}^2$  であり、実施例 8 よりも劣る出力特性であった。電極基材の表面粗さが実施例 8 に比べて粗く、電極触媒層が電極基材にしみ込み、プロトン交換膜と電極触媒との間に良好な接合界面を形成できなかったためと考えられる。

#### 【0083】実施例 9

##### (1) 無機導電性物質分散液の作成

界面活性剤 (TRITON X-114、ナカライテスク (株) より購入)  $12 \text{ g}$ 、アセチレンブラック (DENKA BLACK、電気化学工業 (株) 製、窒素比表面積  $61 \text{ m}^2/\text{g}$ )  $6 \text{ g}$ 、PTFE 水分散液 (ポリフロン PTFE、ダイキン工業 (株) 製)  $2.5 \text{ g}$ 、水  $39.5 \text{ g}$  を混合し、ホモジナイザーで十分にかくはんした。分散液の粘度を高めるため、かくはん中に  $60^\circ\text{C}$  まで加熱し、水分の一部を蒸発させた。得られた分散液の粘度は、 $1600 \text{ Pa} \cdot \text{s}$  であった。

##### 【0084】(2) 電極基材の作成

炭素繊維織物 (E-TEK 製クロス、タイプ A、目付け  $116 \text{ g/m}^2$ ) の片面に (1) で作成した分散液を塗布し、直ちに  $100^\circ\text{C}$  にて乾燥させた。得られた織物のアセチレンブラック付着量は  $2 \text{ mg/cm}^2$  であった。この織物に  $380^\circ\text{C}$ 、 $3 \text{ MPa}$  の圧力をかけ、 $3 \text{ MPa}$  の圧力を保ったまま 15 分間かけて室温に冷却するプレスを行い、電極基材を得た。得られた電極基材の無機導

電性物質が付着している側 (平滑な側) の表面粗さは  $9 \mu\text{m}$  であった。

【0085】(3) 電極触媒層付き電極基材の作成  
上記 (2) で作成した電極基材の無機導電性物質が付着している側に、実施例 1 (3) と同様にして触媒-ポリマ組成物を塗布し、直ちに乾燥して、電極触媒層付き電極基材を作成した。得られた電極触媒層付き電極基材の電極触媒層は、白金の付着量  $0.5 \text{ mg/cm}^2$  であった。

【0086】(4) 膜-電極接合体の作成および評価  
上記 (3) で作成した電極触媒層付き電極基材を用いて、実施例 1 (4) と同様にして膜-電極接合体を作成し、I-V 特性を測定した。最高出力は  $450 \text{ mW/cm}^2$  であり、優れた高出力特性を示した。

#### 【0087】

【発明の効果】本発明により、従来のものに比べて燃料拡散性、排水性がよく、触媒層の浸み込みを抑えることができ、さらに触媒層とプロトン交換膜と間のプロトン伝導性が高い高性能な電極基材およびその製造方法を提供することができる。

#### 【図面の簡単な説明】

【図 1】本発明の電極基材の一実施例の縦断面図である。

【図 2】図 1 の電極基材とは異なる態様の本発明の電極基材の縦断面図である。

【図 3】図 2 の電極基材とは異なる態様の本発明の電極基材の縦断面図である。

#### 【符号の説明】

- 1 …… 多孔質導電シート
- 2 …… 無機質導電性物質層
- 3 …… 電極触媒層
- 4 …… プロトン交換膜
- 5 …… 電極基材 (本発明)

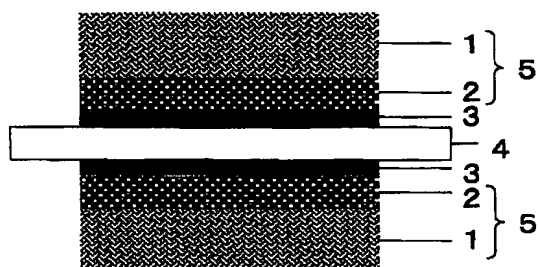
【図 1】



【図 2】



【図3】



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